MINERALIZATION OF BISPHENOL A BY HETEROGENEOUS CATALYTIC OZONATION

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ABSTRACT

Emerging pollutants especially the ones well known as endocrine disrupting compounds (EDCs) have attracted much attention recently due to the toxic effects of these materials even at very low concentration on both animals and humans. Bispenol A (BPA) is an important EDC with very high consumption in industry and also high release to the environment. Among different techniques to remove organic compounds including BPA from water, ozonation is an established method but it is not sufficient to completely mineralize pollutants. As a result, heterogeneous catalytic ozonation offers a promising potential in removal techniques by not only increasing the mineralization of organic compounds, but also decreasing the consumption of ozone and consequently improving the feasibility of process.

The main aim of this study is evaluating mineralization of BPA in non-catalytic ozonation systems and heterogeneous catalytic ozonation processes in the presence of suitable catalysts. More specifically, effect of different parameters in non catalytic ozonation of BPA such as BPA and ozone initial concentration, pH and temperature were investigated. Non-catalytic ozonation was found to be able to accomplish complete degradation of the initial BPA in less than 4 minutes, but unable to convert the by-products of BPA ozonation so that, only 35% conversion of the total organic carbon (TOC) was achieved in 60 minutes.

Adding proper catalysts to system can significantly enhance the efficiency of mineralization. Activated carbon, alumina and Mn- alumina are three catalysts investigated in this project and each of them showed reasonable improvement in term of TOC conversion. Activated carbon mostly suitable good adsorbent and it removed 90 % of BPA in the absence of ozone. On the

other hand, alumina and Mn- alumina were successful in combination with ozone. Catalytic ozonation in the presence of alumina and Mn- alumina attained TOC conversions of about 90 % for both of the cases.

Furthermore it was shown that by changing the catalyst particle size from pellets to powders, TOC conversion increases from 44% to 90% which showed the significant effect of mass transfer limitation due to intra-particle diffusions. Dosage of alumina (0.5 to 4 g/L) did not show a strong effect on the TOC removal. Alumina and Mn- alumina proved to be strong adsorbent for acidic by-products of BPA reaction. Catalyst reusability and deactivation studies indicated that catalysts became deactivated by the adsorption of carbonaceous by-products after few cycles of the reaction in the absence of ozone. Whereas, in the presence of ozone these adsorbed carbons are consistently oxidized by ozone and the catalyst surface remains fresh. A kinetics study was completed for TOC removal of BPA mineralization systems and estrogenicity test indicating that ozonation improves reduction of estrogenicity of BPA, but further decrease can be attained by using alumina as an effective catalyst in ozonation system.

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DEDICATION

*To my mother, **Nahid Shams**, for her endless love, encouragement and support*

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NOMENCLATURE

BOD	Biochemical oxygen demand (mg/L)
C_A	Aqueous concentration of compound A (M)
COD	Chemical oxygen demand (mg/L)
DO	Dissolved oxygen (mg/L)
D_{O3}	Diffusivity of ozone in water ($m^2\ s^{-1}$)
d	Catalyst particle diameter (mm)
E_2	17-β-estradiol
k	Rate constant of the reaction between ozone and compound A ($M^{-1}\ s^{-1}$)
K_L	Ozone liquid side mass transfer coefficient (ms^{-1})
k_{O3}	Reaction rate constant of micropollutant with molecular ozone ($M^{-1}\ min^{-1}$)
k_{OH}	Reaction rate constant of micropollutant with hydroxyl radicals ($M^{-1}\ min^{-1}$)
k_{obs}	Observed reaction rate constant ($M^{-1}\ min^{-1}$)
$\boldsymbol{\eta}$	Effectiveness factor
M_H	Hatta number
pH_{PZC}	pH of point of zero charge
pK_a	Acid dissociation constant
S_{BET}	Catalyst specific surface area ($m^2\ g^{-1}$)
TOC	Total organic carbon (ppm)

ABBREVIATIONS

AOP	Advanced oxidation process
BPA	Bisphenol A (2,2-bis-(4-hy-droxyphenyl)propane)
CHNS	Carbon, Hydrogen, Nitrogen and Sulphur analyzer
EDC	Endocrine disrupting chemical
EFSA	European Food Safety Authority
EPA	Environmental Protection Agency
EU	European Union
HPLC	High performance liquid chromatography
IPCS	International Program of Chemical Safety
NTP	National Toxicology Program
OECD	Organization of Economic and Cooperative Development
WHO	World Health Organization

CHAPTER 1

INTRODUCTION

Public health and protection of the human-living environments is one of the major concerns of all modern governments. However, transmission of various diseases through aquatic routs such as drinking and recreational water and foods produced from polluted water resources is still a problem. The human exposure to wastewater discharged into the environment has also increased in the past decades due to increase in the world population and higher demand for water resources for various purposes [1]. Besides, wastewater reuse has provided a valuable opportunity for protecting the environment by extending the lifetime of available water resources. A considerable diversification of water reuse practices has occurred in the last few years, in areas such as green space and crop irrigation, recreational and various urban uses, and industrial applications [2, 3]. On one hand by developing the world's industry and economy, a lot of new man- made materials have been introduced to the environment and made a massive pollution specifically in water sources. On the other hand, conventional water and wastewater treatments have failed to response to these newly emerged pollutants. So it is the time to improve

the treatment techniques in order to effectively remove these pollutants from our water sources. In this sense, ozonation processes have recently drawn a lot of attention, since ozone is a very strong oxidant with minimum side effects in quality of water. However, catalytic ozonation is even more attractive treatment because of reduction in amount of ozone consumption and consequently improving economical feasibility of treatment processes. Thus, in present work, we focused on complete mineralization of a target pollutant by ozonation in the presence of heterogeneous catalysts.

Endocrine disrupting chemicals (EDCs) that are categorized as emerging contaminants found a huge application in industry and consequently had a high load of release into the environment, in recent years [4,5]. Wide ranges of chemical compounds that are classified as EDCs are capable of disrupting the endocrine systems of animals and humans [6,7]. One of the important EDCs is Bisphenol A (BPA), a well known plasticizer used widely in industry. Therefore, due to public awareness about properties of these pollutants, different actions from governments and environmental agencies towards these emerging micropollutants and also establishment of appropriate methods to distinguish chemicals with estrogenicity effects [8], lots of research groups have been encouraged to study various removal methods for these pollutants. Among various purification techniques ozonation is one of effective methods to remove micropollutants. In this section, three major topics, EDCs, BPA and ozonation will be addressed to provide a general background to understand core concepts of this study.

1.1. Endocrine Disrupting Compounds

EDC have been defined by the Organization of Economic and Cooperative Development (OECD) as "an exogenous substance or mixture that alters the function(s) of the endocrine systems and consequently causes adverse health effects in an intact organism, or its progeny or (sub) populations". There is a wide range of chemical compounds that are capable of disrupting the endocrine systems [6].

Furthermore, the Environmental Protection Agency (EPA) has defined environmental endocrine disrupting compounds (EDCs) as exogenous agents that interfere with the "synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development, and/or behavior " (EPA, 1997) [9]. The effects caused by the presence of EDC in the environment are, reduction in the breakage of eggs of birds, fishes and turtles, feminization of male fish, problems in the reproductive system in fishes, reptiles, birds and mammals, and changes in the immunologic system of marine mammals. In some cases, these effects can lead to decrease of populations. The effects of EDC's in human beings reported so far have been reduction of the amount of sperm, increase of the incidence of breast, testicle and prostate cancers, and the endometriosis [6].

Nowadays, different government and non-government organizations such as the US Environmental Protection Agency (EPA), the World Health Organization (WHO), or the International Program of Chemical Safety (IPCS) are considering this problem and setting up directives and legal frameworks to protect and improve the quality of fresh water resources [6].

1.2. Bisphenol A

Although the estrogenic properties of bisphenol A (2,2-bis-(4-hy-droxyphenyl)propane, BPA) were reported as early as 1936 by Dodds and Lawson, only recently have these properties attracted much attention. Bisphenol A was first synthesized in 1905. It is obtained by reaction of phenol with acetone in the presence of a catalyst. Bisphenol A is a fairly water-soluble compound (300 mg L^{-1} at room temperature) and it dissociates in an alkaline environment (pKa 9.9–11.3) [10]. BPA chemical structure is shown in Figure 1.1.

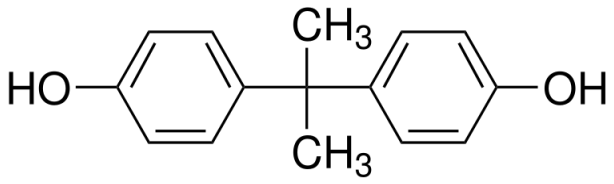

Figure 1.1. Bisphenol A chemical structure

Bisphenol A is mainly used in plastic materials industry, e.g. poly (vinyl chloride), and as an antioxidant in glues, plastics, and ink. In 2001 global production of BPA (started in 1957 in the USA) was estimated to be approximately 2.5 million tons [10], and in 2003 it had over 2 million metric tons global production. From 2003 to 2006, the global BPA consumption increased at an average annual rate of about 10% and the demand for BPA was expected to rise at annual rate of 7–8% during 2006–2011 [9].

Materials containing BPA have been used in many applications, for example as a varnish on the inside of cans and as other packaging used for storage of food products, beverages, and pharmaceuticals. Polycarbonates have been commonly used for production of components of

medical equipment (for dialysis and blood oxygenation), bottles for feeding infants, and kitchen dishes. The wide use of BPA containing polycarbonate polymers follows mainly from their particular properties, light weight, durability, high tensile strength, high modulus of elasticity, high melting point, and high vitrification temperature [10].

For many years BPA was treated as neutral to human health. Detection of BPA in the natural environment, in drinking water, and in food products (since 1990) has, however, aroused the interest of many researchers. At almost the same time the negative effect of this compound on human health was established. Consequently, in 1996 BPA was classified by the European Commission as a substance of external origin with a harmful effect on human health. Numerous toxicological and biochemical studies have confirmed that bisphenol A has estrogenic properties and an agonistic effect toward the estrogenic receptor. In recent studies bisphenol A was classified as chemical disturbing hormonal balance in humans and other animals, a so-called endocrine disruptor. Bisphenol A has been proved to have estrogenic activity even at concentrations below 1 ng L^{-1} [10].

Recently it attracted public attention when several agencies issued reports questioning its safety, especially its application in consumer products used for food and drink packaging. In the U.S., the National Toxicology Program (NTP) released a draft report regarding the adverse effects of BPA exposure on human development and reproduction in April 2008. In the report, NTP expressed the potential effects of BPA exposure using a five-level scale of concern: serious concern, concern, some concern, minimal concern, and negligible concern. On the basis of the concern levels, NTP expressed “some concern” for effects on the brain, behavior, and prostate

gland in fetuses, infants, and children at current BPA exposure levels. The European Food Safety Authority (EFSA) also issued its opinion on the safety of BPA in November 2006. EFSA established a total daily intake of 50 µg of BPA per kilogram of body weight per day. This is on the basis of BPA present in air, food, drink, or water that can be taken daily over a lifetime without significant health risk. In October 2008, the Government of Canada announced that it would immediately proceed with drafting regulations to prohibit the importation, sale, and advertising of polycarbonate baby bottles that contain BPA.

Studies on humans and laboratory animals indicated that BPA causes adverse health effects such as estrogenic potency, liver damage, pancreatic β-cell function disruption, thyroid hormone disruption, obesity-promoting effects, and increases the prevalence of cardiovascular disease, diabetes, and liver-enzyme abnormalities in humans [9].

BPA can be released into the environment through different sources, such as discharge of wastewater and wash water generated from BPA production facilities or consumer product manufacturing facilities that utilize BPA, discharge of effluent from wastewater treatment plant, leaching from consumer products containing BPA at hazardous waste landfill sites, deposition of particulates or dust from BPA production, processing, or storage facilities, and accidental discharge. According to the toxic release inventory database, the total environmental release of BPA in the U.S. was about 770 tons from 2000 to 2006, with average annual release of 110 tons. In 2006, the total environmental release of BPA was 98 tons, with the breakdown in air release of 54 tons, water release of 1.7 tons, and soil releases of 42 tons [9].

There are different reports regarding BPA biodegradation which are somehow in conflict with each other. For instance, Andrew et.al. [11] reported that in aerobic environments such as most rivers, BPA has an environmental half-life of between 4.5 and 4.7 days, being degraded primarily by bacteria, but BPA in seawater can survive for longer time with no degradation and the possibility of BPA contamination on a marine organism can be higher than that on freshwater organism [12]. Moreover, another biodegradability study conducted using manometric respirometry test indicated that BPA degrades slowly, achieving 81–93% BPA degradation in 28 days (experimental details followed the procedures detailed in the OECD 301F test to Good Laboratory Practice (GLP) standards). In a laboratory study with an activated sludge treatment process, about 99% BPA removal was achieved in 14 days [9].

1.3. Ozonation processes as water treatment techniques

Ozonation processes are among advanced oxidation (AOP) methods which are based on generation of hydroxyl radicals (•OH) in water. Ozonation process as an AOP technique is used in water and wastewater treatment processes in order to complete mineralization of pollutants such specific micro-pollutants which are normally very resistant to different stages of conventional treatment systems [14].

At normal conditions, ozone (O_3) is a highly unstable and colorless gas with a density of 1.5 times that of oxygen. It is a powerful oxidizing agent with a redox potential of +2.07 V compared with +1.49 V for hypochloric acid, +1.36 V for chlorine, and +1.25 V for chlorine dioxide. The strong electrophilic nature of the molecule is due to the presence of the third oxygen atom. Ozone attacks most metals except gold and platinum. Gaseous mixtures of ozone

with concentrations greater than about 9%, ignite easily and must be generated on site as required. The solubility of ozone in water is ten times greater than oxygen, but, it decomposes rapidly in water with a half-life of decomposition of order of minutes. Although ozone is a highly toxic gas with an irritating odor, it can be detected by its odor at a concentration of 10 to 20 times lower than that required to cause harmful effects even after long exposure times [15].

Reduction potential of ozone in case of understanding its activity is not that useful so it is better to consider ozone as a very reactive species that can oxidize many organic compounds. This highlights that an appropriate reaction pathway must exist for ozone for it to be able to react with a substrate. Although ozone oxidation reaction may be thermodynamically feasible, kinetic factors govern whether ozone will oxidize a pollutant in a reasonable time frame [1].

Ozone reacts with organic compounds through a direct pathway by molecular ozone and a radical pathway by means of hydroxyl radicals. Under acidic conditions and in the presence of radical scavengers which inhibit the chain reaction and decelerate the decomposition of O_3, the direct ozonation pathway dominates. But under basic conditions or in presence of solutes which promote the radical-type chain reaction which accelerates the transformation of ozone into •OH radicals the hydroxyl radical reactions dominate [13]. Ozone decomposition proceeds through chain reactions including initiation, propagation and termination steps [14]:

- Initiation step:

$$O_3 + OH^- \rightarrow O_2^{\bullet -} + HO_2^{\bullet} \qquad k_1 = 70\ M^{-1}s^{-1} \qquad (1.1)$$

$$HO_2^{\bullet} \leftrightarrow O_2^{\bullet -} + H^+ \qquad pK_a = 4.8 \qquad (1.2)$$

- Propagation step

$O_3 + O_2^{\bullet-} \rightarrow O_3^{\bullet-} + O_2$ $k_2 = 1.6 \times 10^9\ M^{-1}s^{-1}$ (1.3)

$HO_3^{\bullet} \leftrightarrow O_3^{\bullet-} + H^+$ pKa = 6.2 (1.4)

$HO_3^{\bullet} \rightarrow {}^{\bullet}OH + O_2$ $k_3 = 1.4 \times 10^5\ s^{-1}$ (1.5)

$O_3 + {}^{\bullet}OH \rightarrow HO_4^{\bullet}$ $k_4 = 2.0 \times 10^9\ M^{-1}s^{-1}$ (1.6)

$HO_4^{\bullet} \rightarrow HO_2^{\bullet} + O_2$ $k_5 = 2.8 \times 10^4\ s^{-1}$ (1.7)

- Termination step

${}^{\bullet}OH + CO_3^{2-} \rightarrow OH^- + CO_3^{\bullet-}$ $k_6 = 4.2\times 10^8\ M^{-1}s^{-1}$ (1.8)

${}^{\bullet}OH + HCO_3^- \rightarrow OH^- + HCO_3^{\bullet}$ $k_7 = 1.5 \times 10^7\ M^{-1}s^{-1}$ (1.9)

${}^{\bullet}OH + HO_2^{\bullet} \rightarrow O_2 + H_2O$ $k_8 = 3.7 \times 10^{10}\ M^{-1}s^{-1}$ (1.10)

- Overall Reaction

$3O_3 + OH^- + H^+ \rightarrow 2{}^{\bullet}OH + 4O_2$ (1.11)

The ozonation process can be effectively combined with other oxidation techniques such as ultrasonic radiation, UV radiation, γ-radiation, hydrogen peroxide, Fenton oxidation and solid catalysts. Among these methods, combining ozonation with hydrogen peroxide, UV/ultrasonic radiation and catalysts have found more interest.

It has been proved that the capability of ozone in oxidizing various pollutants by direct attack on different atomic bonds such as C-C bond and aromatic will be further enhanced in the presence of hydrogen peroxide due to the generation of highly reactive OH radicals [16]. The rapid dissociation of hydrogen peroxide releases hydroperoxide ions that accelerate the formation of

hydroxyl radicals by attacking the ozone molecules. Thus, the combination of these methods which lead to production of hydrogen peroxide and consequently OH radicals will be beneficial in the treatment of chemicals that show little or no reactivity towards direct attack by ozone molecules [17].

The advantages of the application of ozone in water and wastewater treatments can be summarized as follows [1]:

- Ozone is more effective in destroying viruses and bacteria compared to other materials such as chlorine.
- The contact time needed for effective ozonation is relatively short.
- Due to the rapid decomposition of ozone, no harmful ozone residuals remain in the system.
- There is almost no regrowth of microorganisms after ozonation.
- Since ozone is generated onsite, there are no extra expenses for shipping and handling and related safety problems.
- Ozonation eliminates the need for reaeration due to its effect on increasing the dissolved oxygen (DO) content of the effluent.

However, same as other processes, ozonation has some drawbacks as well. Some of the disadvantages of the ozonation process can be summarized as follows [1, 18, 19]:

- Relatively high cost of ozone generation process coupled with very short half-life of ozone and requirement of absolutely dry air or oxygen input.

- Needing corrosion-resistant material (e.g. stainless steel) for ozonation due to very reactivity and corrosive nature of ozone.

- Not being economical for wastewaters with high levels of suspended solids (SS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), or total organic carbon (TOC).

CHAPTER 2

LITERATURE REVIEW

In this chapter, a review about BPA removal methods will be provided. More specifically, this chapter describes ozonation processes of BPA in absence and presence of catalysts. In addition, a review of the studies that have been reported about kinetics of ozone and BPA is presented.

2.1. Removal methods of BPA

There are many methods to eliminate micropollutants including BPA but the most effective and newly grown techniques are chemical-oxidative processes, also called advanced oxidation processes (AOPs), which are based on the generation of hydroxyl radicals ($^{\bullet}OH$). Advanced oxidation methods can be categorized as i) Ultrasonic cavitation (through sonochemically activated reactions in water resulting in the formation of highly effective oxidizing hydroxyl radicals), ii) Photocatalytic oxidation (using ultraviolet radiation in the range of UV light in the presence of semiconductor catalyst), iii) Fenton chemistry (using reaction between Fe ions and hydrogen peroxide, i.e. Fenton's reagent) and iv) Ozonation that is the most studied oxidation

process [6]. Besides fluorine, the hydroxyl radical is the strongest known oxidant. Hydroxyl radical can oxidize and mineralize almost every organic molecule into CO_2 and inorganic ions. Rate constants for most reactions involving hydroxyl radicals in aqueous solution are usually in the order of 10^6 to 10^9 mol L^{-1} s^{-1} [6]. In addition to these methods, there are other techniques such as chlorination and biological treatment [9, 21]. Chlorination is a very established process in water and waste water treatments which works based on adding chlorine compounds into water.

Basically, the cost of the process, as well as the concentrations and volumetric flow rate of the effluent to be treated, are some of important factors which should be taken into consideration in choosing the appropriate method of removal of micropollutants [6]. However, there are some limitations with some of the above methods. For instant, several studies on the photolysis of BPA reported that the results were somehow disappointing due to the low capacity of BPA to absorb light at 254 nm. Thus, BPA removal after a UV dose of 5000 $mJcm^{-2}$ was only 25% after 120 minutes irradiation [20]. Although biological treatment is recognized as the most economic method to remove and degrade contaminants but in the case of micropollutants, these substances are not completely removed by activated sludge in sewage treatment. Also, only a fraction of these micropollutants can be adsorbed on the biological sludge [6]. Moreover, there are some drawbacks of chlorination in terms of complex by-products of organic compounds, and more importantly, ineffectiveness of chlorine in removing BPA (BPA has about 13 minutes half life in presence of 1 mgL^{-1} of chlorine) [21].

Alternatively, oxidation with ozone is a promising method used to improve the taste and odour of water and also to eliminate the organic and inorganic compounds in water. Although ozone is a powerful oxidant, it reacts slowly with some organic compounds [22]. In the presence of a catalyst however, the ozonation process is more efficient in the degradation of organic compounds .Ozonation finds application in drinking water disinfection, bacterial sterilization and, generally, for organic compounds degradation. However, its application to wastewater treatment is limited due to its high energy demand. On the other hand, the use of ozonation as a pre-treatment process to transform refractory compounds into substances to be removed by conventional methods appears more economically attractive in wastewater treatment [23].

2.2. Non-catalytic ozonation of BPA

As it is discussed previously in background, ozone generally reacts with organic compounds through a direct pathway by molecular ozone and a radical pathway by means of hydroxyl radicals. Under acidic conditions and in the presence of radical scavengers which inhibit the chain reactions and accelerate the decomposition of O_3, the direct ozonation pathway dominates. However, under basic conditions or in the presence of solutes which promote the radical-type chain reactions and accelerate the transformation of ozone into $^{\bullet}OH$ radicals, the hydroxyl radical reactions dominate [6].

The experimental study of the ozonation process for BPA treatment has been performed in batch [24, 25], semi-batch [9, 26] and continuous [27, 28] operations by several research groups. The batch and semi-batch reactors were more popular due to the simplicity of the study of the kinetics of BPA removal in these reactors. For instance, Garoma, et al. [9] have studied the

dependency of the BPA removal on the initial BPA concentration, influent ozone gas dosage, pH and bicarbonate ion concentration in a semi-batch reactor at various operating conditions. They found that BPA removal increases with increasing the dose of ozone and increasing pH up to pH value of 7. It was found that bicarbonate ion had no significant effect on BPA removal [9]. Garoma et.al. also observed a fast reaction between ozone and BPA with complete BPA removal in all of their experiments in about 20 to 30 minutes [9]. The very fast reaction of BPA and ozone can be confirmed by BPA's half life in exposure to ozone which is reported to be 15 ms in the presence of 1 mgL^{-1} ozone. This very short half life of BPA with ozone in comparison to its half life in the presence of 1 mgL^{-1} chlorine which is 13 minutes can reveal the efficiency of ozonation process versus conventional water treatments such as chlorination in removing BPA.

Similar studies have been reported by different researchers on the kinetics of aqueous phase BPA reaction with ozone. Almost all of these works considered a second order kinetic for BPA removal based on some simplifying assumptions and two of most interesting works are explained as examples below.

Garoma et al. [9] made some simplifying assumptions to obtain the observed rate constant for ozonation of BPA. The reaction of BPA with $^{\bullet}OH$ and aqueous ozone during ozonation has been expressed by a well-established second-order kinetics as follows (Eq. (2.1)):

$$\frac{d[BPA]}{dt} = -k_{\bullet OH}[BPA][^{\bullet}OH] - k_{O_3}[BPA][O_3] \qquad (2.1)$$

where $k_{\bullet OH}$ is the reaction rate constant of BPA with $^{\bullet}OH$ and k_{O3} is the rate constant for reaction with aqueous ozone. In order to simplify the rate law, the [$^{\bullet}OH$] and [O_3] can be assumed to be constant during the course of ozonation. Based on this assumption, Eq. (1) can be simplified into Eqs. (2) and (3) as follows:

$$\frac{d[BPA]}{dt} = -k_{obs}[BPA] \tag{2.2}$$

$$ln\frac{[BPA]}{[BPA]_{\circ}} = -k_{obs}t \tag{2.3}$$

where k_{obs} is a pseudo-first-order rate constant for removal of BPA during ozonation and is equal to $k_{OH}[OH\cdot]+k_{O3}[O_3]$, $[BPA]_0$ is initial concentration of BPA, and [BPA] is residual concentration of BPA at time, *t*. The plot of ln ($[BPA]/[BPA]_0$) vs. *t* yields a straight line with the slope of k_{obs}. Assuming that degradation of BPA in the ozonation process primarily occurs by direct reaction with aqueous ozone, the second order rate constant, k_{O3}, can be estimated by dividing k_{obs} by the aqueous ozone concentration. The k_{O3} values varied in the range of $(0.48-2.59) \pm 0.16\times10^5$ M^{-1} s^{-1}. The values obtained in this study are within the ranges of k_{O3} values reported in other reports which is 1.3×10^4 M^{-1} s^{-1} and 2.7×10^6 M^{-1} s^{-1} [9].

In another approach for kinetic study of BPA and ozone, Deborde et.al. [24] performed an extensive work on kinetics of some EDCs including BPA (i.e. 4-n-nonylphenol, bisphenol A, 17α-ethinylestradiol, 17β-estradiol, estrone, and estriol) in variety of reaction conditions such as pH and ozone initial concentration. They conducted some preliminary ozonation experiments in

case of each compound and noticed a very high reaction rate with ozone and so they had to use a comparative method for kinetics study. They used phenol as a competitor compound because of its very similar structure to these of EDCs for kinetics study. Also they used tert-butyl alcohol to avoid radical reactions because the objective of work was to determine the reaction rate constant for ozone molecule only. Interestingly, they reported the reaction rate constant for ozone with neutral and ionized EDCs which can be described as below in the case of BPA:

$$O_3 + BPA \xrightarrow{k1} by - product \quad (2.4)$$

$$O_3 + BPA^- \xrightarrow{k2} by - product \quad (2.5)$$

$$O_3 + BPA^{2-} \xrightarrow{k1} by - product \quad (2.6)$$

It is mentionable that these three states of BPA (Equations 2.4 to 2.6) directly depend on pH of solution and the pKa of BPA. Then they calculated these k1, k2 and k3 for neutral and ionized BPA as 1.68±(0.21) × 10^4 , 1.06±(0.15) ×10^9 and 1.11±(0.52) × 10^9 M^{-1} s^{-1}, respectively [24]. Generally all the reported reaction rate constants for BPA are between 10^4 to 10^9 M^{-1} s^{-1} [9, 24].

Due to the complexity of the reaction between BPA and ozone, leading to generation of different by products that consume ozone, a fixed stochiometric ratio for this reaction is difficult to propose. The ratio obtained based on this method is extremely time dependant so that the results reported in the literature vary in a wide range from 1.5 to 21.1 mole ozone per mole BPA [29, 30].

There is a literature gap about exact intermediates produced during the BPA oxidation by ozone, but there is a work completed by Deborde et al. [21], studying the intermediates of this reaction. They found that ozonation reactions in purified water had shown that the pH of the solution significantly decreased from 6.5 to about 4.5 at the end of the reaction. This may be due to the formation of carboxylic acids. Under their experimental conditions (Milli-Q purified water), five major transformation products were identified according to the mass and UV spectra information. The reaction of ozone would lead, as primary transformation products, to the formation of either 1) muconic acid derivative, 2) benzoquinone, 3) 2-(4-hydroxyphenyl)-propan-2-ol, 4) orthoquinone and 5) catechol, according to already well-described ozone reaction modes. In addition to these major transformation products, other transformation products were also observed. Chemical structures of these minor compounds are still unclear. However, it was suggested that some of them, with high molecular weight and long retention times, could result from secondary reactions between first ozonation products of bisphenol A. Under water treatment conditions, the formation of the observed minor transformation products is probably negligible due to low initial bisphenol A concentrations. Concerning the major transformation products (catechol, orthoquinone, muconic acid derivative, benzoquinone and 2-(4-hydroxyphenyl)- propan-2-ol), low stability of these compounds is expected by considering their variation according to the ozone dose applied. For all these compounds, further transformations giving smaller and more polar compounds (such as acids or aldehydes) are then expected [21].

2.3. Heterogeneous Catalytic Ozonation of BPA

The reaction of ozone with most organic compounds is slow in terms of total carbon conversion. The ozonation process has been found more efficient in degradation of organic compounds in

combination with other techniques or chemicals and one of these successful methods, is ozonation in the presence of active catalysts [3,22,31]. Catalyst as a material to accelerate or decelerate the reaction rate in industry has a huge applications and recently it has been shown that by combination with ozone, they increase efficiency of ozonation processes as well. Alumina and alumina-based catalysts have been reported to be effective in enhancing the removal efficiency of different organic pollutants in the presence of ozone and also they improve economical efficiency of the process by reducing ozone consumption [32–35]. It has been reported that ozonation process can remove most of the micropollutants very rapidly and presence of catalysts does not have a significant effect in term of micropollutants removal but they greatly improve ozone processes in converting the all remaining by-products to water and carbon dioxide [36].

The experimental works involving catalysts are known to be very complex systems to study and there are many issues to be addressed such as the effect of different reaction parameters (solution pH, dose and particle size of catalyst), long term usage of catalyst and its activity in extensive runs of experiments, mass transfer limitation and the mechanism of catalytic reaction. But in ozonation experiments with many primary and secondary intermediate species one has to deal with even more complicated system. So that, studying of each of these factors are crucial to better understand the function of catalyst in ozonation processes [32-37].

Although a number of research groups have worked on BPA removal using non-catalytic oxidation with ozone [9,20,21,24,27,29,30], potential of heterogeneous catalytic ozonation process has remained mostly unexplored [20]. Moreover, majority of the published literature

have focused on the removal of only BPA from water and the remained intermediates of reaction between ozone and BPA have been overlooked. However, alumina-based catalysts have been successfully applied to mineralize phenolic compounds [36,37], so these catalysts could be considered potentially suitable candidates to enhance mineralization of BPA, because of similar structure of BPA to phenols.

Pocostales et.al. [36] used alumina and a synthesized alumina-based catalyst (Co_3O_4-alumina) for removing pharmaceutical compounds, diclofenac, sulfamethoxazole, and 17α-ethynylstradiol (They have phenolic ring in their structure same as BPA.). All of these three pharmaceuticals were removed in less than 10 minutes with direct reaction with ozone. However, remaining COD and TOC after degradation of the compounds confirmed the inadequacy of ozone to mineralize these micropollutants completely. After applying alumina and Co_3O_4-alumina to ozonation systems a clear enhancement in term of COD and TOC removal of these pharmaceuticals was observed. They reported catalytic activity of alumina or Co_3O_4-alumina was probably due to ozone chemisorption and surface decomposition into free radicals and adsorption of some organic compounds that, once adsorbed, could react more easily with ozone [36].

The similarity of BPA structure to the diclofenac, sulfamethoxazole, and 17α-ethynylstradiol supports the possibility of enhancing the mineralization of BPA in the presence alumina and alumina-based catalyst in ozonation systems.

2.4. Research Motivation

Several research projects have been conducted on the elimination of BPA and study of kinetics of different reactions for BPA degradation, including processes based on ultrasonic cavitation, photocatalytic oxidation, Fenton chemistry and ozonation [6]. Although many research groups have worked on BPA removal in ozonation systems, heterogeneous catalytic ozonation was rarely the objective [20] and potentials of low cost and stable alumina based catalysts in degradation and mineralization of BPA have remained unexplored. Thus, the main objective of this work is to investigate the catalytic effects of activated carbon, high surface area alumina and alumina-based metallic catalyst i.e. manganese (Mn) supported on alumina to enhance process of mineralization of BPA by ozone. The results of this study will help to develop valuable knowledge regarding the heterogeneous catalytic ozonation and will be useful in evaluating feasibility of using catalytic ozonation to eliminate micropollutants in water.

2.5. Research Objectives

The main aim of this work is studying the non-catalytic ozonation as well as the effectiveness of three solid catalysts in the catalytic ozonation system to mineralize BPA. The catalysts used in this study are activated carbon, commercial high surface area alumina and synthesized Mn-alumina. For this purpose, the following specific objectives are considered:

- Establish the effect of different reaction conditions such as pH, temperature, ozone concentration and BPA initial concentration on non-catalytic ozonation process and determine the maximum TOC conversion for BPA.

- Perform blank tests such as adsorption of BPA on surface of each of the catalysts in the absence of ozone and also ozone decomposition in the presence of catalysts in the absence of micropollutant.

- Use catalysts under the same reaction condition as non-catalytic ozonation experiments to study the enhancement of BPA mineralization by catalysts.

- Examine long term usage of catalysts in the catalytic ozonation systems to address the question of applicability of catalysts in applying to real water treatment cases.

- Study the estrogenicity and toxicity of reaction mixture before and after non-catalytic and catalytic ozonation processes to ensure that remained compounds after each experiment are harmless.

CHAPTER 3

EXPERIMENTAL

This chapter describes the purchased materials and the preparation methods for other used chemicals such as stock solutions, synthesized catalysts and buffers. Also, the procedures for each type of experiments including, non-catalytic ozonation, ozone decomposition, absorption of micropollutant, catalytic ozonation, and estrogenicity and cytotocicity tests are explained. Finally after introducing analytical methods for different measurements during experiments, reproducibility and uncertainty analysis is presented in this section.

3.1. Materials

3.1.1. Model Compound

The BPA used in this study was supplied from Sigma Aldrich® with more than 99% purity. Other chemicals used in this research were all analytical grade and purchased from either Sigma Aldrich® or VWR. BPA stock solution was prepared using ultra pure Milli-Q water (18 MΩ cm^{-}

[1]). As it is mentioned in background section, BPA solubility is about 300 mgL^{-1} in water so it limits stock solution concentration. In this work, we prepared 200 mgL^{-1} BPA stock solution and by adding specific amount of this concentrated stock solution to the reactor we could reach the desired BPA initial concentration. Regarding initial pH of solution, it has been tried to avoid addition of any buffers unless in case of studying pH effect on mineralization of BPA. The reason for avoiding buffer in this work is using alumina as a catalyst. Phosphate buffers are proved to block alumina's active sites and reduce catalytic activity of alumina. But, in those experiments which pH was the target factor to study, hydrochloric acid was used to set the pH at 2, and phosphate buffers (KH_2PO_4 and K_2HPO_4, 0.05 M ionic strength) were used to set pH at 7. Except for these two pH points, all other experiments were performed at neutral pH of Millipore water which is around 5.7± 0.3 and just set to exactly 5 (by 0.01 M sulfuric acid) to be consistent for all experiments.

3.1.2. Catalysts Preparation and Characterization

Activated carbon Norit ROW powder purchased from Alfa Aesar, was used without any additional treatment. Commercial γ-Al_2O_3 was purchased from VWR in 1/8 inch pellets, and they were crushed and sieved to desired particle size range before use. Mn-Al_2O_3 10 wt% was synthesized from γ-Al_2O_3 by dry impregnation method using manganese nitrate aqueous precursor. The impregnated γ-Al_2O_3 was dried at 100 °C for 10 hours and then calcined at 500 °C for 4 hours. BET surface area was determined for all of our catalysts and the results are shown in Table 3.1.

3.2. Experimental Procedures

Figure 3.1 shows a schematic diagram of the experimental set up. Ozone was produced from pure oxygen by OZV-8S model ozone generator (Ozone Solutions Co). The ozone generator can provide 8 g h^{-1} ozone from pure oxygen feed. The ozone rich gas is then directed to a well-mixed semi-batch water jacketed reactor with 1 liter capacity equipped with a reaction monitoring system comprised of a thermometer, a pH probe and an aqueous phase ozone analyzer. Sampling of the reaction solution during the experiments was conducted at 0, 1, 5, 10, 20, 30 and 60 minutes of the reaction period. Concentration of ozone in the outlet stream was measured by ozone gas analyzer and then ozone was destroyed by an ozone destruction unit (ODS-2 Ozone Solutions). All experiments were started upon attaining a targeted aqueous ozone concentration in Milli-Q water that is initially charged into the reactor. More details on procedure of each type of experiments are presented in the subsection below.

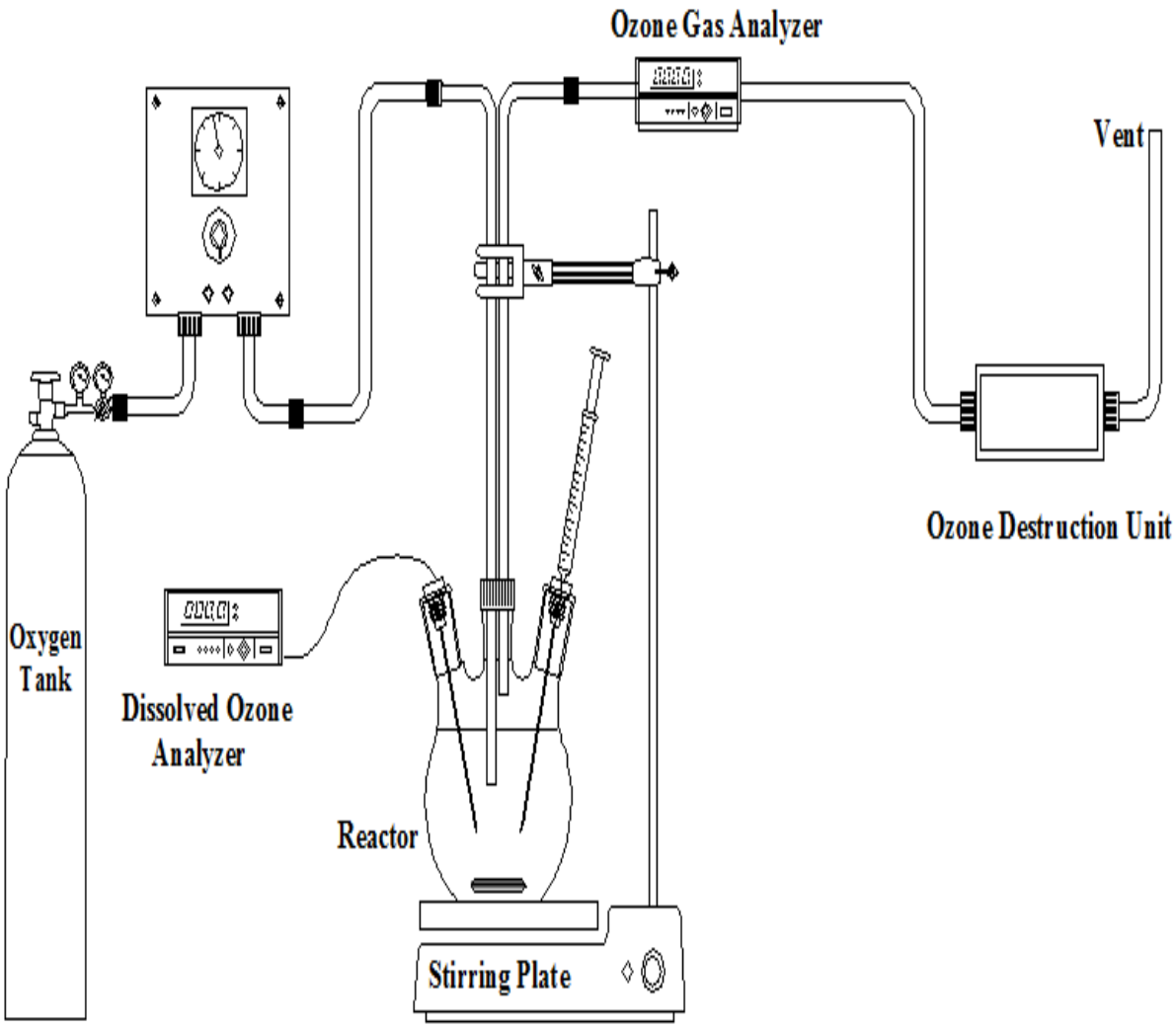

Figure 3.1. Schematic of the experimental Setup

3.2.1. Non- catalytic ozonation of BPA in different reaction conditions

Non-catalytic ozonation experiments were designed to test ability of ozone alone to mineralize BPA under different reaction conditions. So the experiments were performed in order to study four different factors, BPA initial concentration effect, ozone initial concentration effect, pH effect and temperature effect. However, according the results that we obtained in non-catalytic ozonation experiments we set a reaction condition as a reference condition for all other types of

experiments including adsorption, ozone decomposition and catalytic ozonation. Reference reaction condition can be was: aqueous ozone concentration= 4.5±0.5 ppm (9.4×10^{-5} M), BPA concentration= 10±1 ppm (4.4×10^{-5} M), pH= 5±0.1 and temperature= 23±2 ˚C. These conditions have been kept the same in all experiments except those experiments which each of the factors (ozone concentration, BPA concentration, pH and temperature) was the target factor to study.

Generally after establishing the desired aqueous phase ozone concentration in Milli-Q water, a carefully controlled volume of the concentrated stock solution of BPA was added to the reactor to obtain the desired initial BPA concentration. The time of adding BPA to reactor was considered the zero time for reaction and after that, periodic samples (20 ml) were taken from reactor. Immediately after withdrawing samples from the reactor, they were introduced to 0.05 M $Na_2S_2O_3$ to destroy residual aqueous ozone in the sample and stop further reactions.

3.2.2. Adsorption of BPA on surface of catalysts

This set of experiment was performed to test the adsorption capacity of catalysts (γ-Al_2O_3, Mn-Al_2O_3 and activated carbon) towards BPA in absence of ozone. Similar to reaction conditions as non-catalytic ozonation reference experiment (without any ozone in the system), specific amount of catalyst was added to reactor and then in specific time intervals samples were withdrawn to test for BPA and TOC concentration. In runs with catalyst, the samples were first filtered by syringe filters with Supor® Membrane (Pall® Life Sciences) with 0.2 µm pore size. These syringe filters are compatible with BPA or generally TOC of reaction solution and no measurable loss of BPA and TOC were observed due to these filters.

3.2.3. Ozone decomposition

Ozone decompositions tests were performed in order to study the effects of catalysts (γ-Al_2O_3 and Mn-Al_2O_3) on aqueous ozone concentration. This effect contributes to decomposing ozone to even stronger species such as OH radicals. The experiments were performed under same reaction conditions as reference conditions in non-catalytic ozonation experiments, but without presence of micropollutant (BPA). After ozonating Milli-Q water and reaching the specific concentration of aqueous ozone in the reactor, 1 gL^{-1} catalyst was added to the ozonated water. Then the changes in the concentration of ozone were tracked by monitoring ozone concentration every 2 seconds by ozone probe.

3.2.4. Catalytic ozonation of BPA

In case of catalytic ozonation experiments, known amount of the catalyst (γ-Al_2O_3 and Mn-Al_2O_3) was added to the system simultaneously with the BPA stock solution under reference reaction conditions as non-catalytic experiments. Same as adsorption experiments, in catalytic ozonation runs, the samples were first filtered by syringe filters with Supor® Membrane before analyzing with HPLC and TOC system. It is mentionable that catalyst particle size is a very important factor in catalytic ozonation reactions and we studied the effect of different ranges of particle size from 4 mm to fine powder with less than 0.2 mm diameter in the case of γ-Al_2O_3. Dose of catalyst is another important factor which should be addressed in catalytic reactions. Dosage of alumina catalyst is studied as well as its particle size.

3.2.5. Toxicology tests

The estorogenicity and cytotoxicity evolutions have been conducted in collaboration with Toxicology Research Centre and Department of Veterinary Biomedical Sciences, University of Saskatchewan. The method for estrogenicity tests were based on MCF-7 cells (breast cancer cells) for the detection of estrogenic activity of BPA untreated and treated samples. The MCF-7 cells were modified by assaying the reporter enzyme activity of firefly luciferase to cell line called MVLN. By this modification, these MVLN cells in exposure to estrogenic compounds radiate light which is detectable by plate-scanning luminometer and then it is easily related to estrogenicity level using comparison with a standard estrogenic compound, usually 17-β-estradiol (E_2). The more detailed procedure can be found elsewhere [8].

3.3. Analytical Method

3.3.1. BPA and TOC concentrations

An Agilent 1200 series HPLC was used to measure concentration of BPA in the solution. The column for separation was Eclipse plus C18 (4.6×150 mm, 5 μm) and the column temperature was 40 °C. A DAD detector with a wavelength of 280 nm was used and the mobile phases were 60% water and 40% acetonitrile with 1 ml min^{-1} flow rate and 500 μl injection volume. In order to measure total organic carbon (TOC) content of samples, a TOC-VCSH SHIMADZU automatic TOC meter which operates based on the combustion of the organic compounds in the sample was used. TOC meter was calibrated with standard solution of potassium hydrogen phthalate each time before analyzing the samples.

3.3.2. Ozone concentration, pH and temperature

Reaction monitoring system comprised of a thermometer, a pH probe (R-27012-06, Cole-Parmer Inc.), an aqueous phase ozone analyzer (MS-08, AMT Analysenmesstechnik, GmbH) and gas phase ozone analyzer (Teledyne M465M). The aqueous ozone analyzer can record ozone concentrations in the reaction medium every two seconds. These readings were logged into a computer using a data acquisition system (cDAQ-9172, National Instruments Corp).

3.3.3. Catalyst properties

BET surface area measurements were performed by physi-sorption of N_2 at 77 K using an ASAP 2000 system (Micromeritics Instrument Corp.). Elemental analysis was performed using Vario EL III CHNS elemental analyzer to measure the percentage of Carbon (C), Hydrogen (H), Nitrogen (N) and Sulphur (S) adsorbed on the catalysts.

CHAPTER 4

NON CATALYTIC OZONATION OF BPA

The result of BPA mineralization with ozone without any catalyst is discussed in this section. The effects of the aqueous ozone concentration, BPA initial concentration, pH and temperature were studied on the TOC removal of BPA in aqueous solution. Each of these parameters is reported separately in this chapter but to give a general sight to BPA mineralization just in the presence of ozone an experiment is shown as a reference experiment in the case of non-catalytic ozonation of BPA.

The variation of the aqueous ozone concentration and TOC removal as a function of reaction time is shown in Figure 4.1. This process is under reaction conditions of aqueous ozone concentration 4.5±0.5 ppm, BPA concentration 10±1 ppm, pH 5.0 ± 0.2 and temperature 23±2 ˚C that is decided to be kept constant as reference conditions for all other catalytic experiments. As can be seen in Figure 4.1, the maximum TOC removal of 35% was achieved after 60 minutes reaction. The reaction proceeds very fast for the first 10 minutes upon introduction of BPA into

the reactor leading to fast consumption of aqueous ozone and also fast removal of TOC. Despite low conversion of total carbons in ozonation experiments, the l HPLC analysis showed that BPA was degraded within the first 4 minutes of the reaction (Figure 4.2). Fast disappearance of BPA in the system, is in accordance with very high reaction rate constant for the ozone and BPA reaction reported to be in the range of 1.3×10^{4} M^{-1} s^{-1} and 2.7×10^{6} M^{-1} s^{-1} [6]. Fast reaction between ozone and some other aromatic compounds has also been reported by others [21, 36].

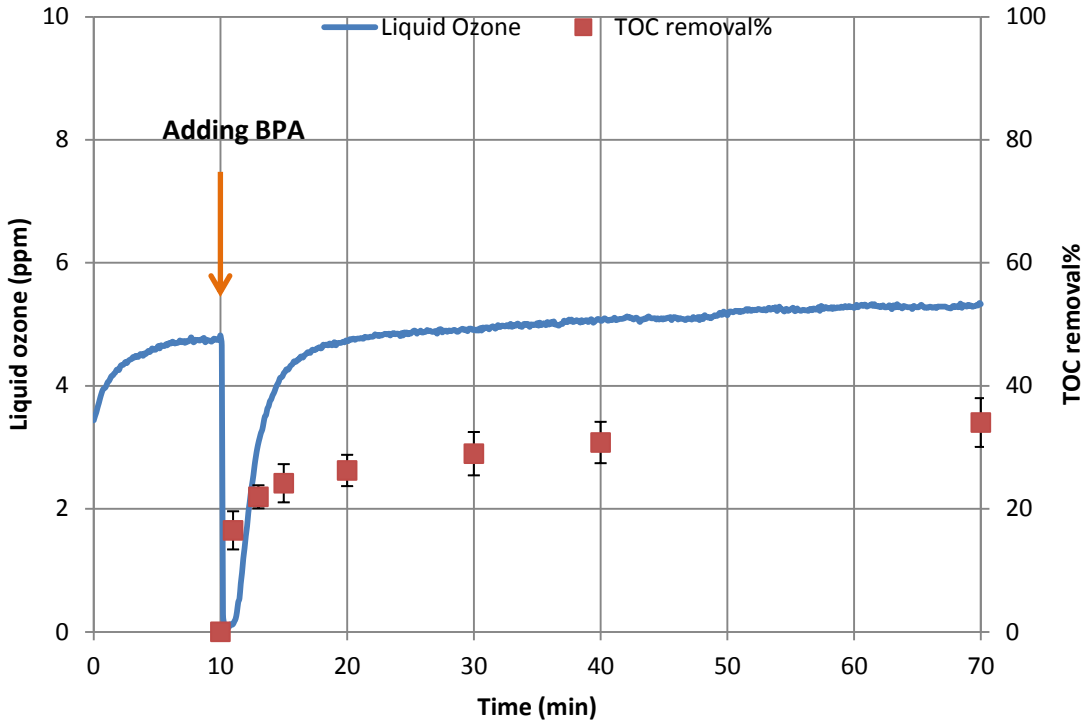

Figure 4.1. Aqueous ozone concentration and TOC removal in non-catalytic ozonation ($[BPA]_0$=10±1 ppm,$[O_3]_0$=4.5±0.5 ppm, pH_0= 5.0 ± 0.2 , T=23±2 ˚C), error bars represents STD error for TOC removal percentage.

During the reaction, pH of the solution dropped from 5 to 3.6 after one hour ozonation. This can be attributed to the formation of final non-degradable linear acidic by-products during the ozonation process. Deborde et al. [21] reported that muconic acid derivatives, benzoquinone, 2-(4-hydroxyphenyl)-propan-2-ol, orthoquinone, catechol compounds and acids or aldehydes are possible by-products of BPA ozonation. The leveling-off of the TOC curve even after long reaction times indicates that non-catalytic ozonation only leads to incomplete mineralization of BPA, producing linear acidic by-products which cannot be removed by ozonation.

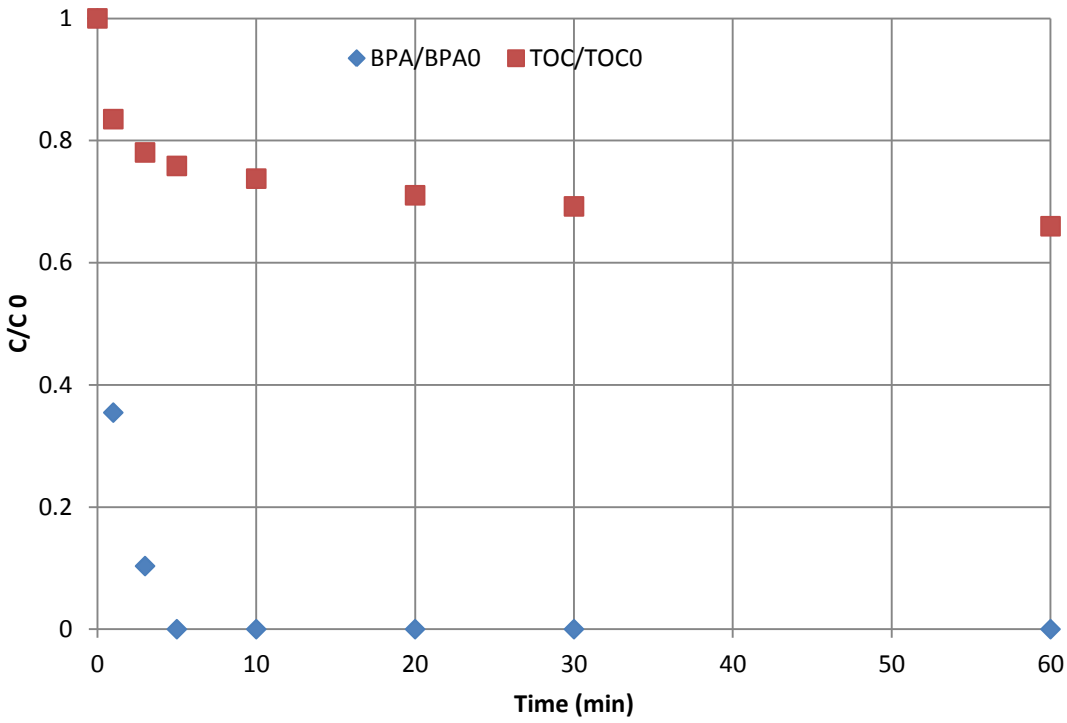

Figure 4.2. BPA concentration and equivalent TOC concentration ($[BPA]_0$=10±1 ppm, $[O_3]_0$=4.5±0.5 ppm, pH_0= 5.0 ± 0.2 , T=23±2 ˚C).

To evaluate reproducibility of ozone and TOC concentrations, non-catalytic ozonation experiment under reference reaction conditions, were repeated five times. The experimental error

in measurement of TOC concentration was found to be less than 5%. Aqueous ozone initial concentration showed even less error about 2% in the repeat experiments. The standard deviation of data samples for TOC is presented in Figure 4.1.

The effect of BPA initial concentration, aqueous ozone concentration, pH and temperature on mineralization of BPA in ozonation systems are presented as follows.

4.1. Effect of BPA initial concentration

The effect of initial BPA concentration at 5, 10 and 20 ppm on the TOC removal of aqueous BPA was investigated. The aqueous ozone concentration, pH and temperature were kept constant at, 4.5±0.5 ppm, 5.0 ± 0.2 and 23±2 ˚C, respectively. As it is shown in Figure 4.3, there is a very slight difference regarding TOC removal for different initial concentrations of BPA, however, it is showing less decrease when BPA is 20 ppm in the system. This means that the same amount of ozone (4.5±0.5 ppm) is not enough to mineralize 20 ppm of BPA as much as 5 or 10 ppm BPA. Moreover, by paying more attention to the trend of TOC removal in non-catalytic ozonation experiments, two completely different phases can be distinguished. First phase is from the beginning of the reaction till about 10 minutes of reaction time, with very fast reaction rate primarily between ozone and BPA and then between ozone and BPA's by-products. As can be seen in Figure 4.1, initial dissolved ozone was consumed as soon as BPA was added to system and the entire gaseous ozone entering reactor continued to be consume either by remaining BPA or its by-products. But once reactions fell to second phase which is a very slow reaction towards most probably linear by-products of BPA, aqueous ozone started to accumulate in the reactor and finally after about 10 minutes of reaction it again reached to its stable value in the reactor.

Interesting point about ozonation system of BPA is that, regardless of reaction conditions these two phases were observed in all our experiments. The reason for poor dependency of TOC removal to initial concentration of BPA can be explained by this two-phase reaction nature of BPA and its by-products with ozone. In the beginning of the reaction the initial concentration of BPA can affect the removal percent, and as can be seen in Figure 4.3, in the first phase of reaction, TOC removal is significantly different for different BPA concentrations, but as reaction proceeds this difference was reduced by time. The same trend for BPA removal with ozone in different BPA initial concentrations was reported by Garoma et.al [9].

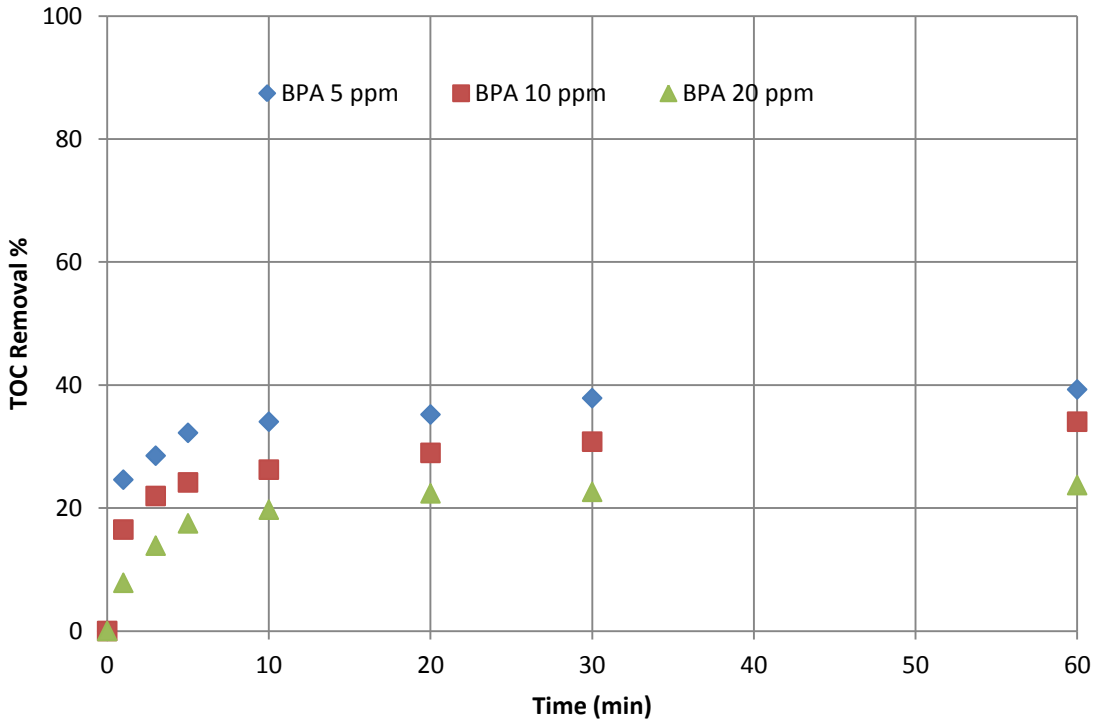

Figure 4.3. Effect of different initial concentration of BPA on TOC removal ($[BPA]_0$=5, 10 and 20 ppm,$[O_3]_0$=4.5±0.5 ppm, pH_0= 5.0 ± 0.2 , T=23±2 ˚C)

4.2. Effect of ozone initial concentration

The effect of aqueous ozone concentration of 1, 2, 4 and 8 ppm was evaluated under the same reaction conditions of BPA initial concentration of 10±1, pH of 5.0 ± 0.2 and temperature of 23±2 ˚C. The results of TOC removal versus reaction time are shown in Figure 4.4 for this set of experiments.

As it can be seen in Figure 4.4, the trend for removal of TOC for various initial ozone concentrations is similar to BPA initial concentration effect. However, again the differences are not significant, but higher concentration of ozone result in higher TOC conversion as well. The two reaction phases are valid for these experiments, too.

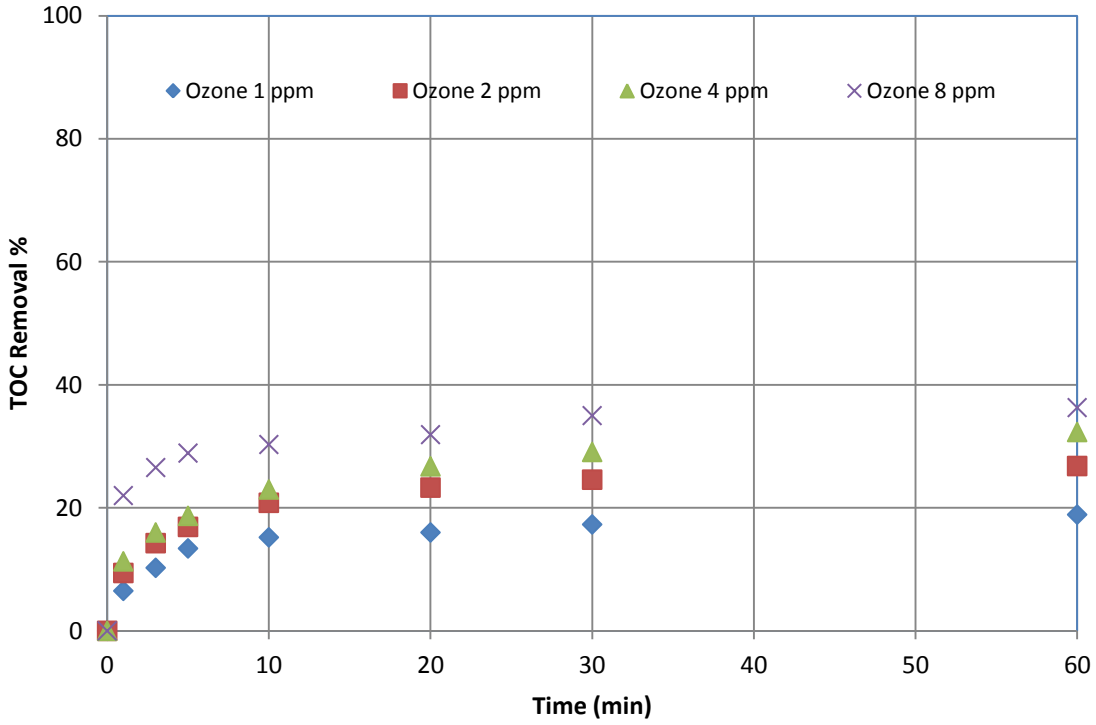

Figure 4.4. Effect of different initial concentration of ozone on TOC removal ($[BPA]_0$=10 ppm, $[O_3]_0$=1, 2, 4 and 8 ppm, pH_0= 5.0 ± 0.2 , T=23±2 ˚C)

4.3. Effect of pH

To better understand ozone oxidation process of BPA, some experiments were performed at different pH values of 2, 5 and 7. Since ozone decomposition rate and consequently its gas-liquid concentration equilibrium values strongly depend on pH of solution, study of pH effect on mineralization of BPA is very important. Figure 4.5 represents effect of reaction solution pH on removed percent of TOC for BPA under the reference reaction conditions of our work (BPA initial concentration of 10±1 ppm, ozone concentration of 4.5±0.5 ppm and temperature of 23±2 ˚C).

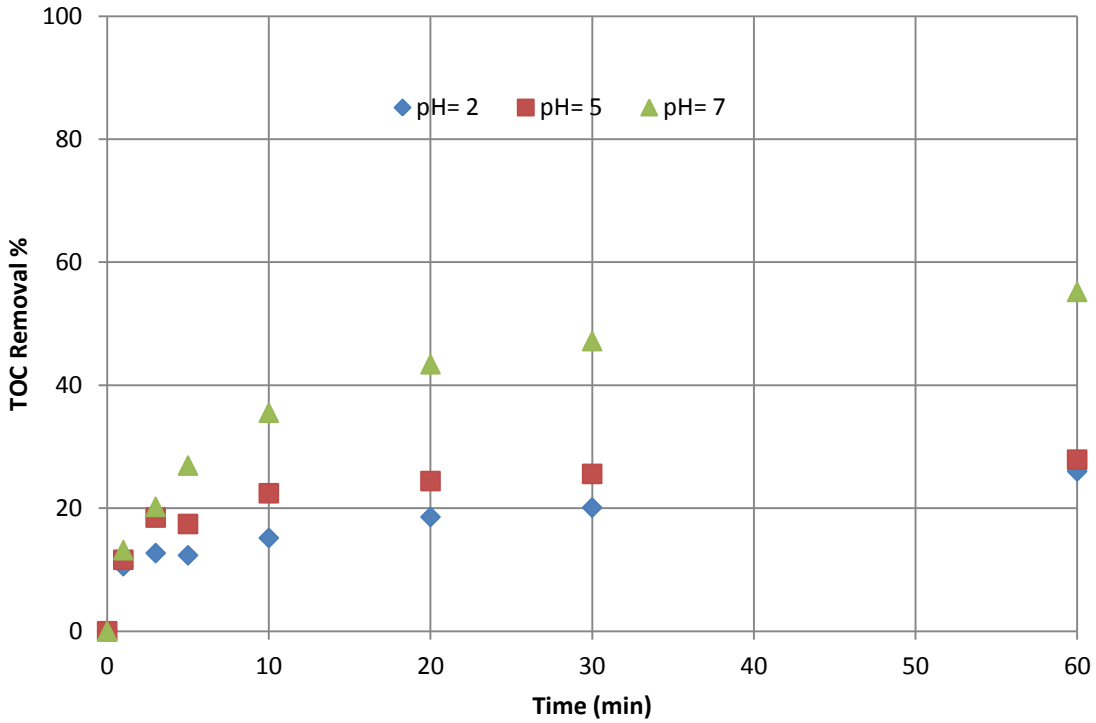

Figure 4.5. Effect of different initial pH on TOC removal ($[BPA]_0$=10 ppm,$[O_3]_0$=4.5±0.5 ppm, pH_0=2, 5 and 7, T=23±2 ˚C)

When ozonation experiments were performed at natural pH for Milli-Q water, about 5.7 (adjusted to 5 by dilute sulfuric acid), pH dropped to 3.5 as reaction proceeded during experiment (shown in Figure 4.6). This drop in pH value can be attributed to formation of final linear acidic by-products of BPA and ozone [21]. Then two pH values below and above this pH 5 were studied to evaluate pH effect on the ozone concentration and TOC removal. According to results from Figure 4.5, at acidic pH of 2 final TOC removal was the least among other pH values. This is because decomposition of ozone to OH radicals occurs very slowly and at this pH, organic compounds react mainly with molecular ozone itself [9]. The reason for this phenomenon could be explained by larger amount of H^+ ions in the low pH solutions that can either inhibit the formation or quench the formed OH radicals. In the contrary, at pH value of 7, more OH radicals were formed and consequently TOC removal increased up to 60%.

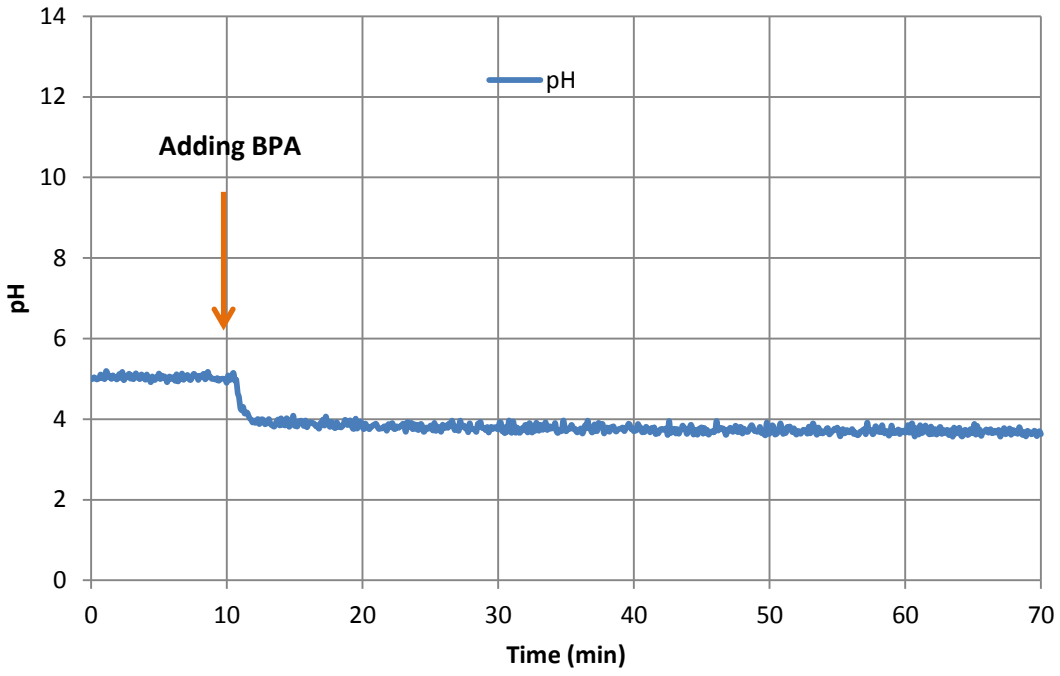

Figure 4.6. Change of pH value during ozonation of BPA ($[BPA]_0$=10 ppm,$[O_3]_0$=4.5±0.5 ppm, pH_0= 5.0 ± 0.2, T=23±2 ˚C)

4.4. Effect of temperature

Experiments were performed at different temperatures to examine TOC removal by changing the temperature of reaction solution. Figure 4.7 shows the TOC removal versus time at three different temperatures of 5, 23 and 35 ˚C. As can be seen in this figure, raising the temperature had a slightly positive effect in the removal reaction of TOC. However, less than 5% difference for each two consequent temperatures revealed that reaction of BPA and its by-products by ozone was not dependant on temperature. This fact makes the process of BPA mineralization easier since temperature is the first factor that can be constant at room temperature for all other experiments in this study.

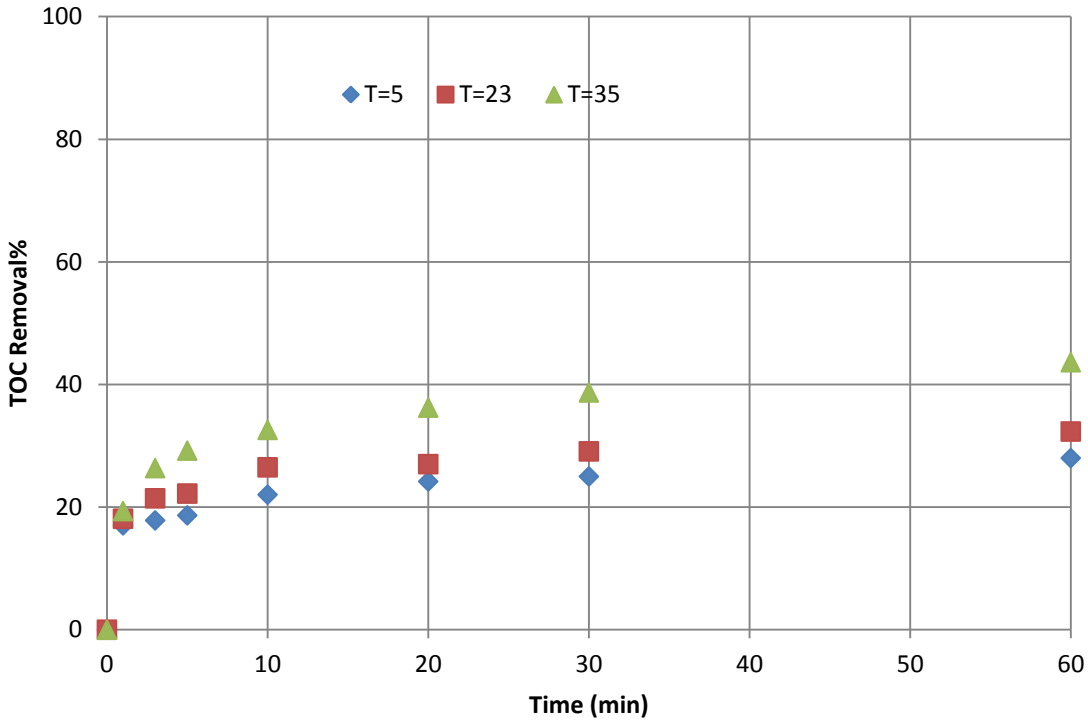

Figure 4.7. Effect of different temperatures on TOC removal ($[BPA]_0$=10 ppm,$[O_3]_0$=4.5±0.5 ppm, pH_0= 5.0 ± 0.2 , T=5, 23 and 35 ˚C)

4.5. Summary and conclusion

In this chapter, the results of study of non-catalytic ozonation of BPA to investigate different factors effects on mineralization process were presented. The general observation for these experiments is a very fast reaction in the first 10 minutes of reaction leading to fast conversion of BPA and almost 27% removal of TOC. But TOC removal improved just about 10% in the rest 50 minutes of reaction with ozone. The results and conclusions of these studies can be summarized as below:

- Both BPA initial concentrations and ozone initial concentrations slightly affect final TOC removal of BPA solutions. However, as expected, lower BPA concentrations as the reactant and higher concentrations of ozone as the oxidizer had positive effect on TOC removal of system.

- pH as an important factor on self-decomposition of ozone in water affects TOC removal of BPA solutions more significantly. At low pH values ozone decomposition is slower and the main reactions are between organic compound and molecular ozone. In contrast, at higher pH values because of generation of more OH radicals TOC conversion was higher.

- Temperature is not a very effective factor in mineralization of BPA in the range of from 5 to 35 ˚C.

CHAPTER 5

CATALYTIC OZONATION OF BPA

In the non-catalytic ozonation experiments we attained only 35% mineralization of BPA, although BPA itself is converted in the first 4 minutes of reaction. The main goal of this study is finding an effective process to increase mineralization of BPA. So that, under the same experimental conditions of reference non-catalytic ozonation experiment, aqueous ozone concentration 4.5±0.5 ppm, BPA concentration 10±1 ppm, pH 5±0.1 and temperature 23±2 ˚C, catalysts were added to the system to study the effect of catalyst on mineralization of BPA. The charachterization of catalysts used in this study is presented in Table 5.1.

Table 5.1. Characterization of catalysts

Catalyst	**Loaded metal (wt%)**	**S_{BET} ($m^2 g^{-1}$)**	**Pore Size (Å)**	**pH_{PZC}**
Activated carbon	-	925	19	9.8
γ-Al_2O_3	-	223	75	7.7
Mn-Al_2O_3	10	171	119	6.6

In this chapter different aspects of reaction of three catalyst candidates, activated carbon, alumina and Mn-alumina are discussed. Physical adsorption of micropollutant on surface of catalysts in absence of ozone, ozone decomposition of catalysts in absence of BPA, ozonation of BPA in the presence of ozone, by-products adsorption on surface of catalysts and finally reusability of catalysts in long term usage are the important catalytic topic that are discussed in this section.

The combination of each of these catalysts, activated carbon, alumina and Mn-alumina, with ozonation process to mineralize BPA is a novel work that has not been reported in the literature. Therefore, it has been developed a step by step procedure to first of all simplify the process in order to evaluate one single factor's effect and second with the obtained results it is possible to move forward and address another possible reason or explanation to the observed phenomenon. For instant, in the beginning it was defined to do specific known experiments such as adsorption, ozone decomposition and catalytic ozonation. But after observing a significant improvement in catalytic ozonation experiments, it was necessary to suggest a reason to this result. So a novel procedure was suggested to test adsorption of by-products on surface of catalysts. The details of each of these experiments with their results are presented in this chapter.

5.1. Adsorption of BPA on surface of catalysts

Adsorption of BPA on surface of the catalysts was studied to evaluate the activity of catalysts in removing BPA in the absence of ozone. Experimental conditions and procedure were kept the same as non-catalytic ozonation reference conditions, except there was no ozone flow to the system and 1 g/L of catalyst was added to study only adsorption capacity of the catalyst towards

BPA. Since it is reported that phosphate buffers block some active sites of alumina catalyst [36], the experiments were carried out in ultra pure water without buffer. The detailed results for each of the catalysts are presented below.

5.1.1. Adsorption of BPA on activated carbon

As it is shown in Figure 5.1, activated carbon in the absence of ozone in adsorption experiment of BPA, showed a significant removal capacity and it adsorbed 90 % of BPA as soon as it was added to BPA solution. However, adsorption process was continued for about 1 hr contact time to observe any possible desorption with time. It is clear in Figure 5.1, adsorbed BPA stayed on the catalyst and final TOC removal after 1 hr remained 90%. It is mentionable that, using this catalyst contributed a considerable amount of TOC addition into the reaction solution in the presence of ozone, resulting in overloading the calibrated range of TOC measurement. Because of high adsorption capacity and contribution to TOC reading of the system, it was decided to discontinue study of activated carbon as a potential catalyst for ozonation of BPA.

Although activated carbon proved to be a very good adsorbent in the case of BPA, generally adsorption process is a physical method which only captures the organic compounds in the pores of the porous catalyst without converting them and eventually after a period of time, saturation of surface pores occurs and there is need for further activation processes for adsorbent. Because of all these factors the best way in case of catalysts is finding a suitable catalyst to not only adsorb the organic compounds but also to promote reaction between pollutants and oxidizing agent, in this work ozone.

5.1.2. Adsorption of BPA on alumina and Mn-alumina

As it is shown in Figure 5.1, there is no significant adsorption of BPA on alumina after 1 hr and the final adsorption of TOC was less than 10%. Thus, it was concluded that alumina catalyst is a fairly poor adsorbent for BPA. This observation is in the agreement with the reports in literature indicating poor adsorbing ability of alumina and alumina based catalysts in the case of aromatic and phenolic compounds [36], it was expected in the case of BPA, since BPA is an aromatic compound with two phenolic rings.

Interestingly, Mn-alumina showed even less adsorption towards BPA than alumina itself, in exactly same experimental conditions after 1 hr. The reason could be related to loading 10% manganese metal on surface of alumina in Mn-alumina catalyst. The final adsorption in the case of Mn-alumina was less than 5% TOC removal from a 10 ppm BPA solution. As it is presented in Table 3.1, after loading 10% manganese to alumina the surface area of synthesized catalyst dropped from 223 to 171 $m^2 g^{-1}$. So most probably, this decrease in the surface area could result in the less adsorption capacity of synthesized Mn-alumina, as it is observed in Figure 5.1.

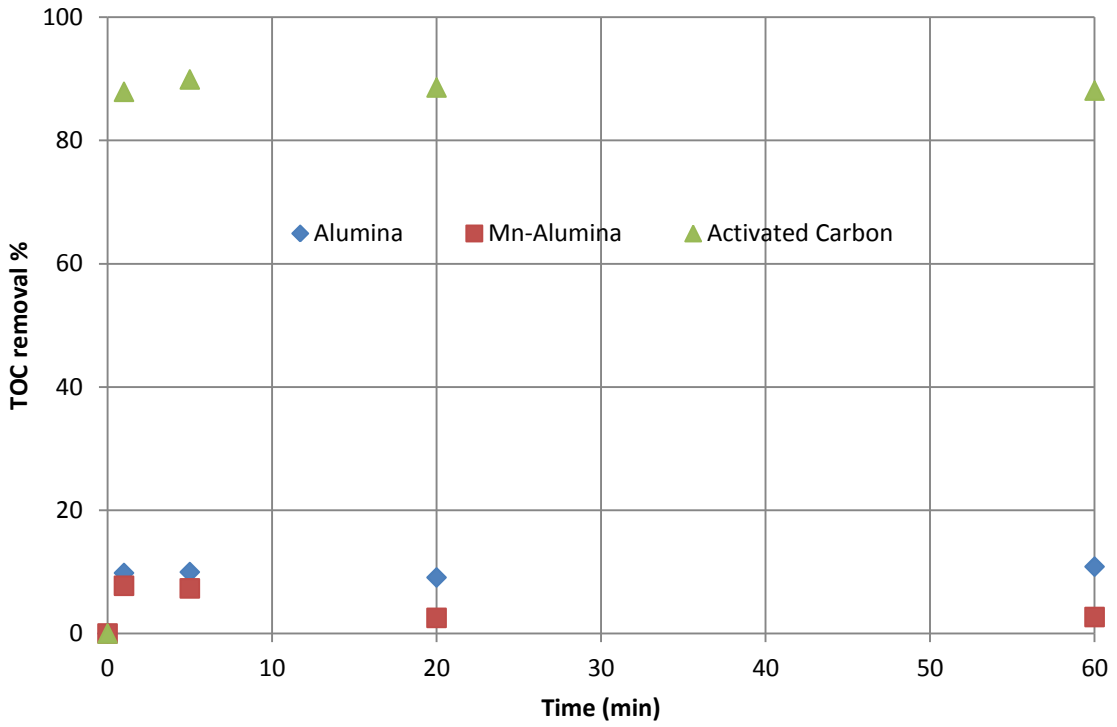

Figure 5.1. Adsorption of BPA on activated carbon, alumina and Mn-alumina catalysts ($[BPA]_0$=10±1 ppm,$[O_3]_0$=0 ppm, pH_0= 5.0 ± 0.2 , T=23±2 ˚C, dose of catalysts= 1 g/ L, particle size of the catalysts< 0.23 mm).

5.2. Ozone decomposition with alumina and Mn-alumina

An indication of performance of catalyst is its capability in decomposing ozone. The ozone decomposition experiments were performed in order to better understand the function of catalyst. In ozone decomposition experiments, aqueous ozone concentration is compared before and after introducing catalyst to the system in the absence of pollutant. This type of experiment has been performed in case of two catalysts, pure alumina and synthesized Mn-alumina to compare the function of loaded metal, manganese, in the catalytic behavior of alumina.

It is important to consider that ozone has self decomposition in water to other species including OH radicals, as discussed in literature review before. But the purpose of these experiments was enhancing this self decomposition with the aid of a suitable catalyst.

As Figure 5.2 illustrates, after adding alumina catalyst to stabilized ozonated water, it showed no effect on decomposing ozone into oxygenated species (e.g. hydroxyl radicals). Some pervious works on alumina catalyst suggested that alumina decomposes ozone to produce OH radicals [34, 38]. However, Pocostales and et al [36] indicated that alumina catalyst alone, cannot transform molecular ozone into hydroxyl radicals. Accordingly in this study, aqueous ozone concentration which remained constant before and after adding alumina confirmed that alumina itself without presence of organic pollutant was not able to decompose ozone to hydroxyl radicals.

The same procedure was repeated in the case of Mn-alumina, but as it is clear in Figure 5.2 that after adding 10% Mn on alumina, the synthesized catalyst can clearly enhance decomposition of ozone to possibly produce OH radicals. The drop in aqueous ozone concentration was about 1 ppm from around 4.5 ppm to 3.5 ppm. It seems that loading a transient metal such as manganese enables the catalyst to directly decompose ozone

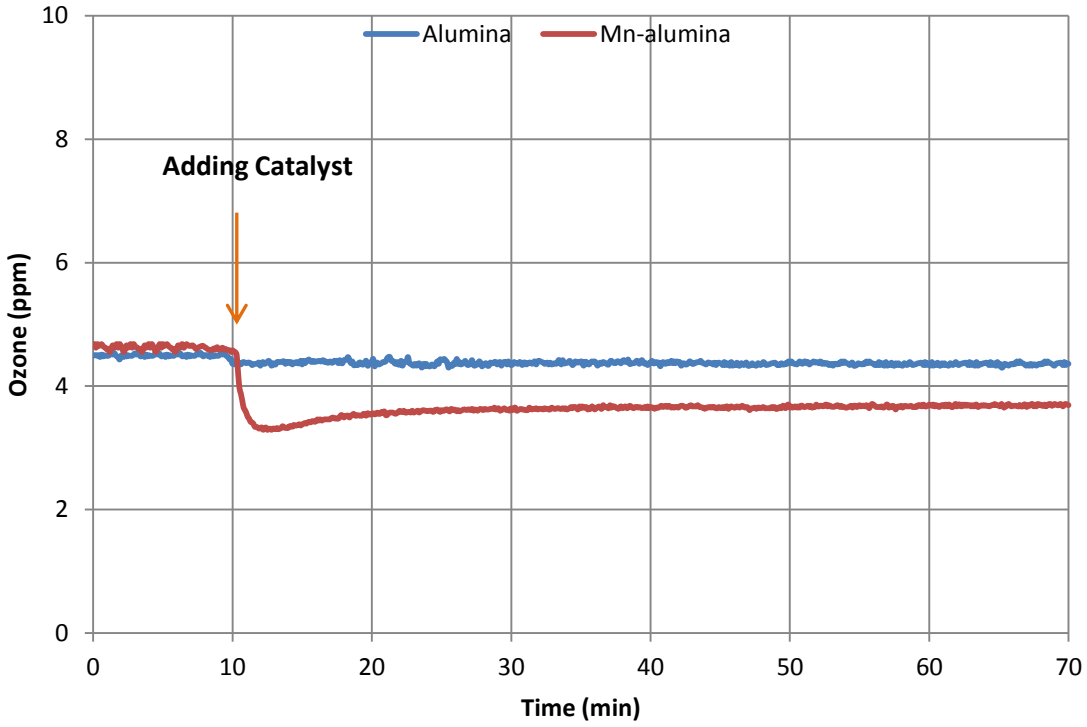

Figure 5.2. Ozone decomposition on alumina and Mn-alumina catalysts ($[BPA]_0$=0 ppm, $[O_3]_0$=4.5±0.5 ppm, pH_0= 5.0 ± 0.2 , dose of catalysts=1 g/ L, particle size of catalysts=powder (d< 0.23 mm))

5.3. Catalytic ozonation of BPA with alumina and Mn-alumina

The main aim of catalytic ozonation experiments was to evaluate the performance of catalyst in improving the mineralization of BPA by catalytic ozonation reaction. In this regard some experiments were performed under the same experimental conditions as non-catalytic zonation reference conditions which were aqueous ozone concentration 4.5±0.5 ppm, BPA concentration 10±1 ppm, pH 5.0±0.2 and temperature 23±2 ˚C. The only difference in these experiments was addition of 1 gL^{-1} alumina and Mn-alumina to the ozonation system.

Figure 5.3 illustrates the TOC removal with time for three cases of ozonation of BPA without catalyst and ozonation with alumina and Mn-alumina catalysts. As can be seen, under the same operating conditions, adding alumina and Mn-alumina catalysts to the system significantly improved the TOC removal.

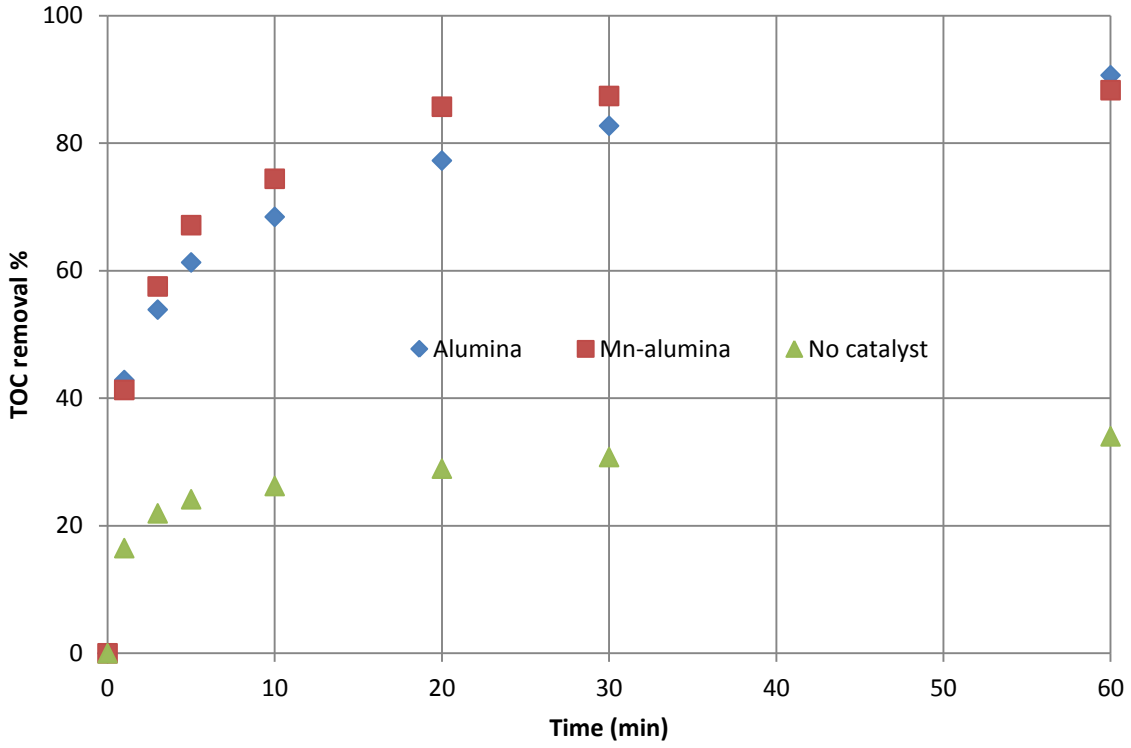

Figure 5.3. Catalytic ozonation of BPA by alumina and Mn-alumina catalysts ($[BPA]_0$=10±1 ppm, $[O_3]_0$= 4.5±0.5 ppm, pH_0= 5.0 ± 0.2 , dose of catalysts= 1 g/ L, particle size of the catalysts<0.23 mm)

The TOC removal after 60 minutes was found to be around 35% for non-catalytic ozonation which has increased to 90% and 85% for alumina catalyzed and Mn-alumina catalyzed ozonation, respectively. The fast conversion in the first 10 minutes of the reaction is most likely due to degradation of the aromatic reaction intermediates by ozone molecule [21, 36]. Pocostales

et al. [36] concluded that the reactions between ozone and diclofenac, sulfamethoxazole and 17α-ethynylstradiol are fast at the beginning of the reactions. A similar trend is observed here. After formation of the linear compounds, reaction rate slows down and levels-off once about 10% of the initial TOC remains in the solution in case of alumina and Mn-alumina catalyzed systems. It is clear that both of the catalysts can enhance the final mineralization of BPA in comparison to non-catalytic ozonation.

So far Mn-alumina followed a very similar behavior to pure alumina in the catalytic experiments and so it was decided to study the effect of different factors such as particle size, dosage and reusability only for alumina. Therefore, in order to develop a more clear understanding of the reaction behavior, effects of catalyst particle size, dosage and activity and reusability in case of alumina catalyst were also investigated.

5.3.1. Effect of alumina particle size

One of the factors which should be addressed in catalytic reactions is the effect of the active surface area and mass transfer limitation on the reaction rate. These two parameters are directly related to the catalyst particle size. Thus, five different catalyst sizes of pure alumina catalyst including pellets (particles with the diameter of 3.00- 4.00 mm), particles in the range of 2.00-2.38 mm, 1.00-1.70 mm, 0.50-0.85 mm and catalyst powder (particles with less than 0.23 mm diameter) were used to degrade 10.0 ppm BPA. The experimental conditions were kept the same as non-catalytic ozonation reference experiment, aqueous ozone concentration 4.5±0.5 ppm, BPA concentration 10±1 ppm, pH 5±0.1 and temperature 23±2 ˚C. Figure 5.6 shows the TOC removal in the presence of 1.0 g/L alumina catalyst with different particle sizes. As can be seen

in Figure 5.4; TOC removal increases from 44 % to 90% by changing the alumina catalyst particle size from 3.00- 4.00 mm to powder size, this may be contributed to the less exposed surface area for BPA.

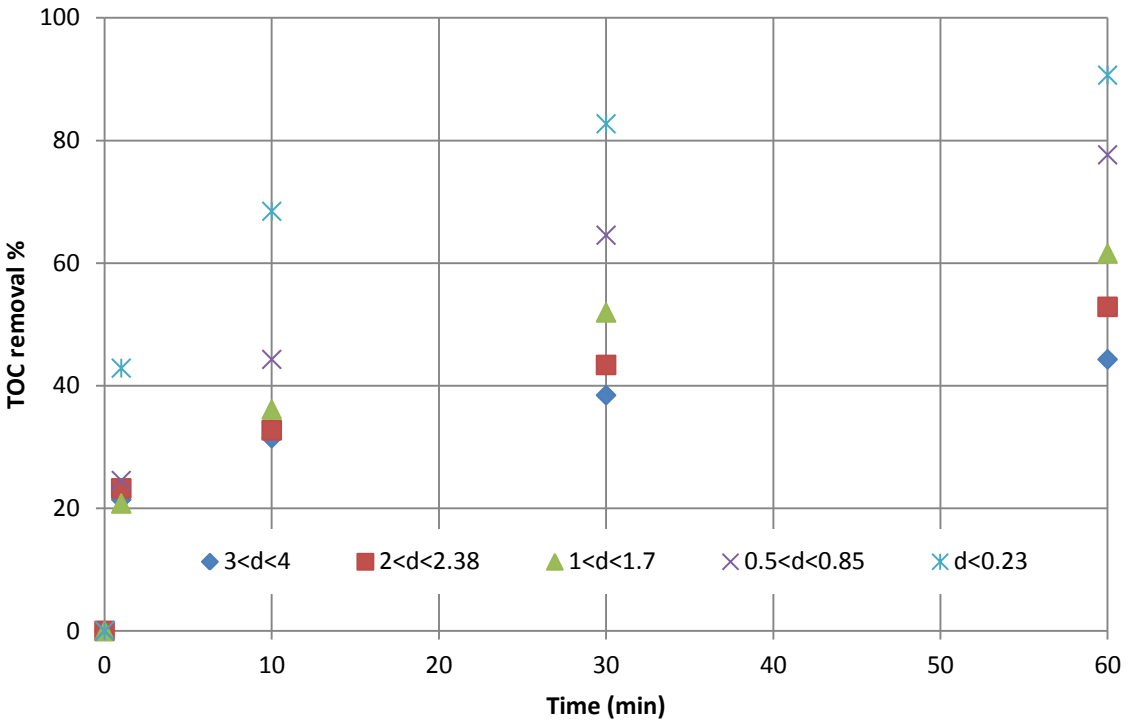

Figure 5.4. Effect of particle size in catalytic ozonation of BPA by alumina ($[BPA]_0$=10±1 ppm, $[O_3]_0$= 4.5±0.5 ppm, pH_0= 5.0 ± 0.2 , dose of catalysts= 1 g/ L)

5.3.2. Effect of alumina dosage

The variation of TOC removal with reaction time for different catalyst dosages is provided in Figure 5.5. According to Figure 5.5, the final TOC removal for 0.5, 1 and 4 g/ L alumina with particle size of less than 0.23 mm, is 74, 90 and 90%, respectively

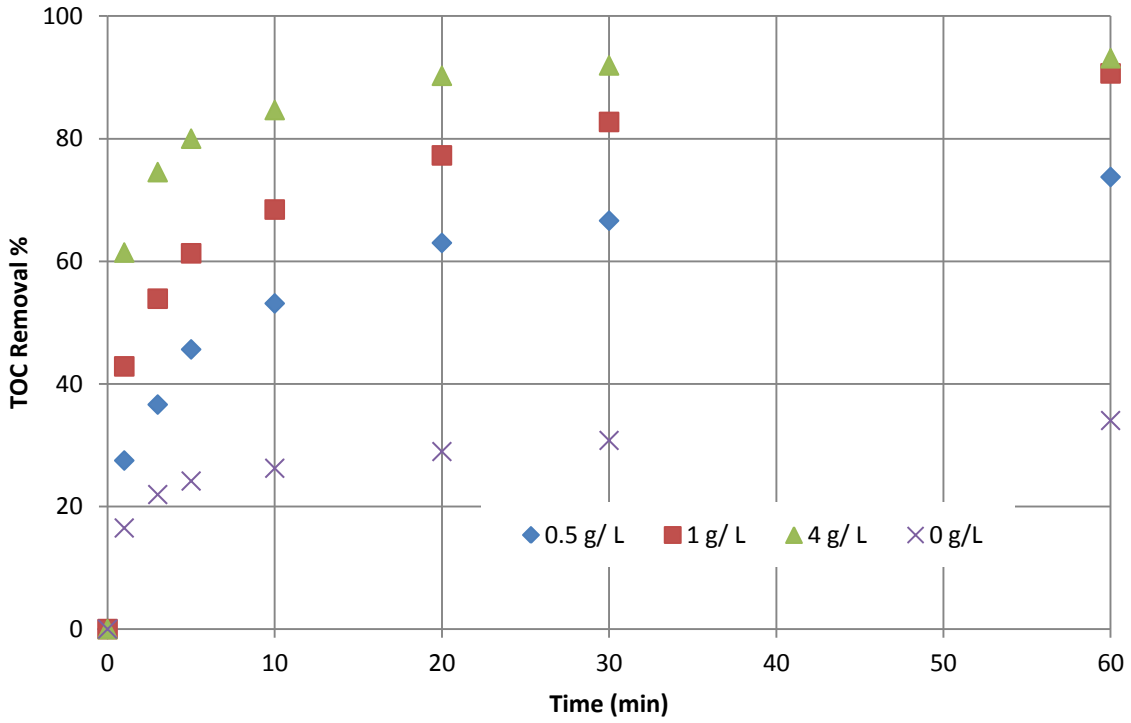

Figure 5.5. Effect of catalyst dose in catalytic ozonation of BPA by alumina ($[BPA]_0$=10±1 ppm, $[O_3]_0$= 4.5±0.5 ppm, pH_0= 5.0 ± 0.2 , particle size of catalyst<0.23 mm)

Although the difference is noticeable in the case of TOC removal at early times of the reaction, they finally reach to the same ultimate TOC removal for 1 and 4 g/L of catalyst. This finding indicates that 1g of alumina catalyst provides sufficient surface area needed for the same amount of BPA and increasing the amount of catalyst by a factor of four does not improve the final mineralization. A similar result has been reported in the case of catalytic ozonation of phenol with alumina-based catalyst by Udrea and Bradu [37]. They observed the same trend for degradation of 2-nitrophenol in presence of different CuO-alumina catalyst dosages.

A reaction kinetics evaluation is presented in next chapter for each of these experiments with different particle size to understand the effect of this factor on rate of BPA mineralization, as well. To exclude the mass transfer limitation effects on the reaction rate, the smallest catalyst particles were used in the rest of catalytic experiments in this work.

5.4. By-products adsorption on surface of alumina and Mn-alumina

After observing significant improvement that catalysts make in mineralization of BPA and also the results obtained from particle size and dosage of alumina catalyst, it was essential to find possible mechanism for this considerable difference made by catalysts. A unique experiment was designed to study adsorption affinity of catalysts towards the formed by-products of BPA during ozonation process. The by-product adsorption experiment is a two-step experimental procedure which in the first step, a non-catalytic ozonation was performed for 1 hr to convert BPA to its ultimate by-products. The reaction conditions were the same as the non-catalytic ozonation reference experiment. 30 minutes after completing the first part, when aqueous ozone concentration dropped to zero, the second step of the experiment was started by adding 1 g/L alumina or Mn-alumina catalysts powder (less than 0.23 mm diameter) to the reactor. Catalyst was left in the reactor for another 1 hr without ozone flowing into the system. Figure 5.6 illustrates the variation of TOC removal with time for each of the two catalysts in this two-step process. Interestingly, the results show around 87% and 82% final TOC removal for alumina and Mn-alumina catalysts, respectively. This clarifies that the contribution of these catalysts in overall ozonation is not only due to their catalytic interaction with ozone, but also due to the direct adsorption of the reaction by-products on the catalysts.

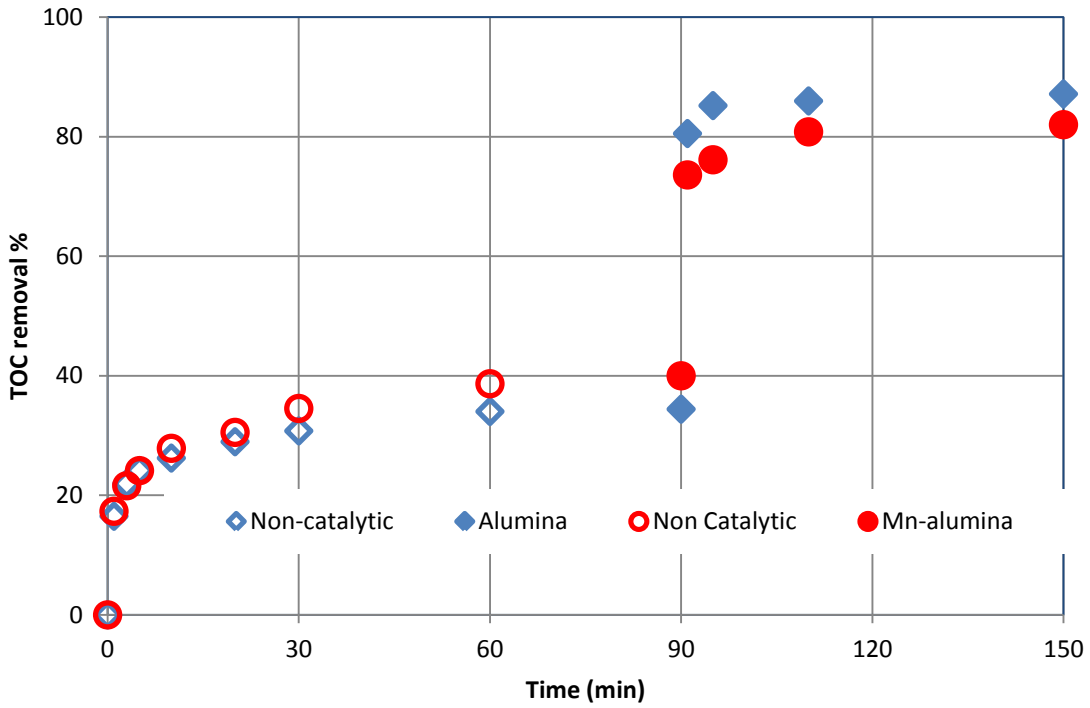

Figure 5.6. By-product adsorption on the surface of alumina and Mn-alumina ($[BPA]_0$=10±1 ppm, $[O_3]_0$= 4.5±0.5 ppm, pH_0= 5.0 ± 0.2 , particle size of catalysts <0.23 mm)

A CHNS analysis was performed on the unused alumina and the alumina used in the reactions. Table 5.1, shows the percent of Carbon (C), Hydrogen (H), Nitrogen (N) and Sulphur (S) content on alumina catalyst before any treatments, after catalytic ozonation and after adsorption of by-products in the absence of ozone. As shown in Table 5.1, percentage of hydrogen, nitrogen and sulfur elements did not changed considerably. However, carbon content on unused alumina was 0.321 % but after catalytic ozonation it increased to 0.822 % and it increased even more after adsorption of by-product to about 1.121 %. This indicates that in the presence of ozone, alumina catalyzes the reaction with less adsorption of by-products and consequently remains more active and fresh. In other words, when alumina catalyst is in the presence of ozone, adsorbed by-products on surface of catalysts react with ozone species and lead to further mineralization. In

catalytic ozonation, accumulation of organic compound on the surface of alumina catalyst was least and further conversion to harmless materials such as water and carbon dioxide took place. However, the by-products adsorption role in the catalytic experiments is still very important.

To confirm the hypothesis of the dual effects of catalyst on reaction (oxidation with ozone and adsorption of by-products), alumina catalyst further reusability and stability experiments were performed both in catalytic ozonation and two-step by-product adsorption process which are presented in the next section.

Table 5.2. Percentage of CHNS elements captured on alumina catalyst before treatment, after catalytic ozonation and after adsorption of by-products

Element	**C (wt%)**	**H (wt%)**	**N (wt%)**	**S (wt%)**
Fresh alumina	0.321	0.995	0.027	0.068
Alumina after Catalytic ozonation	0.822	0.956	0.046	0.057
Alumina after by-product Adsorption	1.121	0.996	0.043	0.046

5.5. Activity and reusability of alumina

Catalyst reusability and deactivation studies were performed using 1g/L alumina with particle size of 1.00-1.70 mm in three consecutive cycles with an initial ozonation of 20 ppm BPA and three successive cycles for adsorption of the by-products. The results of these experiments are shown in Figure 5.7. As can be seen in Figure 5.7 (a), no significant reduction in TOC removal was observed after three ozonation cycles. However, the results for adsorption of by-products, Figure 5.7 (b) show a noticeable decrease after third cycle, indicating that alumina catalyst in the absence of ozone loses its activity. This can be attributed to the deactivation of alumina after adsorption of the carbonaceous reaction by-products (TOCs) in the solution. Whereas, in the presence of ozone these adsorbed carbons are consistently oxidized by ozone and the catalysts surface remain fresh.

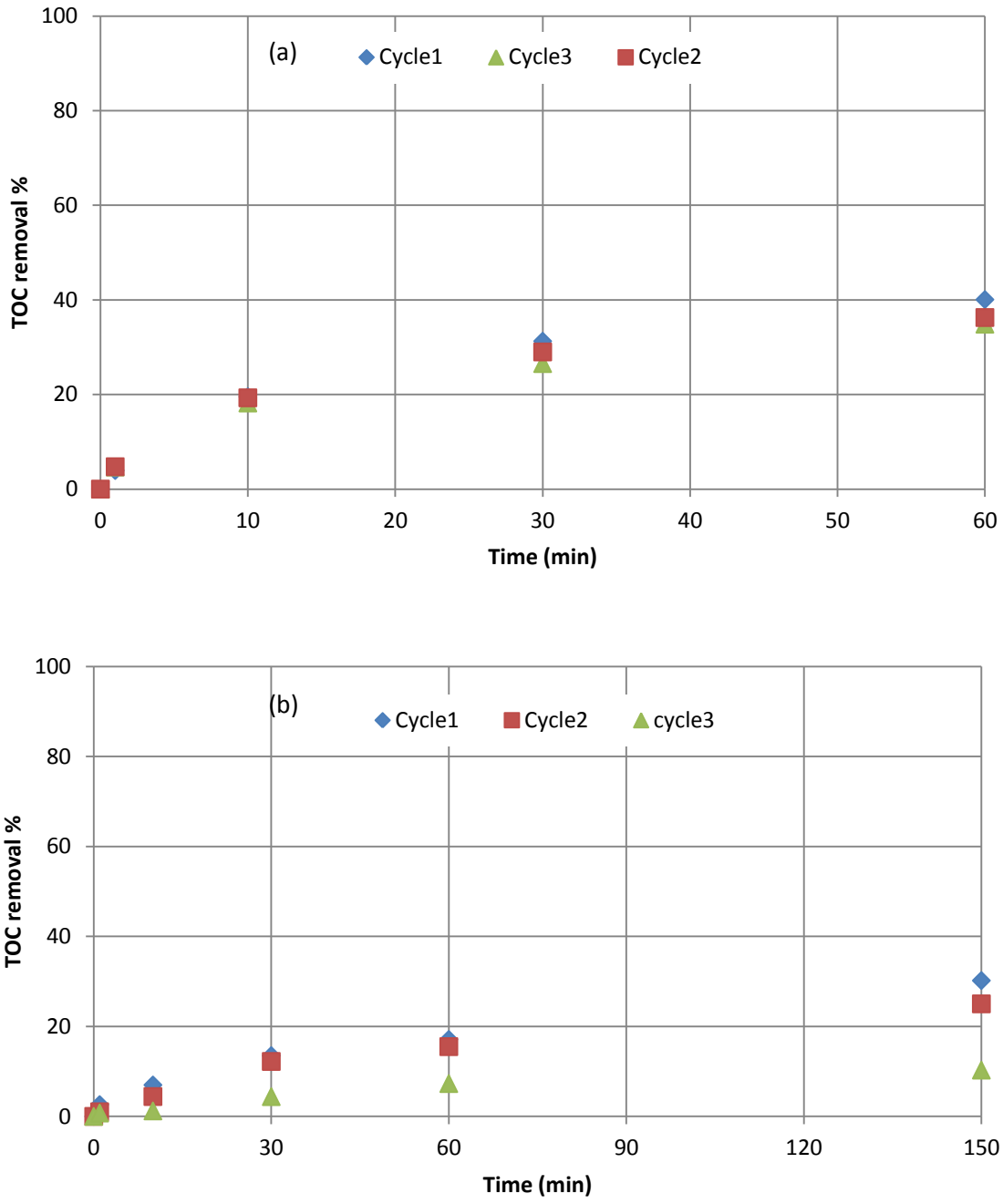

Figure 5.7. (a) Reusability of alumina in catalytic ozonation of BPA ($[BPA]_0$=20±1 ppm, $[O_3]_0$= 5.5±0.5 ppm, pH0= 5.0 ± 0.2 , particle size of catalyst <0.23 mm), and (b) by-product adsorption of 60 minutes ozonated BPA ($[BPA]_0$=20±1 ppm, $[O_3]_0$= 0 ppm, pH0= 5.0 ± 0.2 , particle size of catalyst <0.23 mm).

5.6. Summary and conclusion

Experiments with presence of catalysts showed major results as summarized below:

- Activated carbon showed very strong adsorbing capacity towards BPA and once it was added to solution it adsorbed 90% of BPA and this amount remained constant for another hour.

- Both alumina and Mn-alumina poorly adsorbed BPA in 1 hr of adsorption process (less than 10% TOC removal).
- Alumina is unable to decompose molecular ozone to other oxygenated species most probably OH radicals. In fact aqueous ozone concentration remains the same with or without addition of alumina.

- Loading 10% manganese to alumina enables it to make a difference in decomposition of ozone to other species such as OH radicals in solution.

- Mineralization of BPA in ozonation system can be improved from 35% to 90% by adding alumina or Mn-alumina to the system.

- Particle size of alumina has a strong effect on final mineralization of BPA mostly due to mass transfer limitations. The difference between the largest and smallest particle sizes of alumina was from 44 to 90% for BPA mineralization, respectively.

- The final TOC removal of BPA solution did not show a strong dependence on alumina dosage. TOC removal was 75, 90 and 90% for 0.5, 1 and 4 gL^{-1}, respectively.

- Both of catalysts, alumina and Mn-alumina adsorb a considerable amount of by-products of BPA ozonation.

- CHNS analysis confirmed that alumina catalyst in the presence of ozone with less adsorbed carbon in the same mineralization percent was more successful in compare to alumina in by-products adsorption.
- Alumina catalyst did not show any deactivation after three consequent cycles in the presence of ozone in BPA mineralization catalytic processes.

- Alumina catalyst which showed a very high adsorption of by-products in the absence of ozone failed to serve as a long term adsorbent in the absence of oxidizing agent, ozone. After second cycle the activity of alumina in adsorbing by-products dropped drastically.

CHAPTER 6

KINETICS OF BPA OZONATION

As it mentioned before, kinetics study for ozonation systems of BPA requires specific reaction conditions since the reaction of ozone and BPA is very fast [24]. Although there are a number of reports regarding BPA removal [9, 24, 29], TOC removal was rarely the objective for kinetics study [20]. The nature of advanced oxidation reactions of organic compounds in water matrixes is very complicated due to constant formation of many species such as free radicals or different compositions of organic materials during their breakdown. More specifically, as it is discussed before, on one hand ozone has a self decomposition in water which produces hydrogen peroxide and $OH^{\bullet}$ radicals. On the other hand, the presence of solid catalysts in ozone oxidation of pollutants makes the reaction solution even more complex in term of kinetics study of mineralization of organic compounds due to interaction of surface species on the catalyst with ozone decomposition products and BPA oxidation intermediates.

Although some research groups such as Beltran and coworkers [39, 40], tried to study the kinetics of oxidation of total organic carbon in the ozonation systems; there are still variety of complicated aspects that have not been considered yet in regard to TOC kinetics in such reactions. Therefore, in present work it has been tried to simplify the reaction conditions by involving minimum number of species in the reaction solution (e.g. buffers or $OH^{\bullet}$ radical scavengers) and treat TOC as a distinct compound. One should pay attention to the fact that TOC is a very general term in case of organic compounds which includes species from aromatic compounds with high reactivity towards ozone to large linear compounds with very low tendency to react with ozone as an example Deborde et.al [21] identified five major by-products during ozonation of BPA but they reported that there are more than these five major intermediates and there are a lot of minor primary intermediates during the ozonation of BPA.

The reaction between TOC and ozone can be investigated from two points of views: 1) reaction of TOC and ozone is a fluid-fluid (gas-liquid) reaction without considering solid catalyst involved in the reaction pathway and 2) reaction of TOC and ozone is depending on solid catalyst as a surface on which reaction is taking place. The first subsection below (6.1. Reaction rate constant for BPA ozonation) is describing the first viewpoint and the second subsection (6.2. Mass transfer in catalytic ozonation of BPA) analyses the kinetics based on the second viewpoint. It is worth mentioning that, due to complexity of aqueous phase reaction especially with a compound such as ozone which itself decomposes to other oxygenated species (e.g. hydrogen peroxide, OH radicals, etc), proposing a general mechanism is almost impossible. However, both of mentioned viewpoints in this study can help develop a better understanding of these complex reactions.

6.1. Reaction rate constant for BPA ozonation

In fluid-fluid reactions such as gas (ozone) and liquid (dissolved BPA) reactions, both mass transfer and chemical reaction are important. To recognize the role of each of these terms, a dimensionless parameter called Hatta number can be defined for the system as [41]:

$$M_H = \frac{\sqrt{K D_{O3} C_A}}{K_L} \quad (6.1)$$

Where, k, D_{O3}, C_A and K_L are rate constant of the reaction between ozone and compound A, diffusivity of ozone in water, aqueous concentration of compound A, and ozone liquid side mass transfer coefficient, respectively. Because of unknown nature of other by-products in ozonation of BPA, it is possible to calculate Hatta number for the initial reaction of ozone and BPA. The terms in the formula of Hatta number are reported for ozone molecule in the literature as D_{O3}= 1.3×10^{-9} m^2 s^{-1} and K_L= 5×10^{-5} ms^{-1} [40]. Also there are various research groups that worked on kinetics of ozone and BPA and have reported reaction rate constant, k for ozone and BPA under the reaction conditions close to experiments conditions in this work as, 9.4×10^4 M^{-1} s^{-1} for pH value of 5 [9, 29]. So with these values the calculated Hatta number for ozonation of 10 ppm (4.38×10^{-5} M) BPA is about 1.5, at the beginning of the reaction where decomposition of BPA takes place. This shows that reaction of ozone and BPA is very fast, and it is in agreement of our experimental result for aqueous BPA concentration. The fact that liquid ozone concentration drops to almost zero at the beginning of the reaction is another observation that supports fast rate of reaction compared to mass transfer of ozone.

By considering TOC removal trend and liquid ozone concentration in the system, and also by calculating parameter such as Hatta number for initial and known state of system, one can assume that reaction between ozone and different organic compounds that are forming in different stages of the reaction can be divided into three main phases.

The first stage of the reaction is considered to be the first two minutes of the reaction where high concentration of BPA and initial ozone and a very fast reaction is observed occurring in bulk liquid and possibly in the interface of liquid and gas phases. As it is clear in Figure 4.1, in the first stage of reaction ozone concentration dropped to zero in almost two minutes, also as Figure 4.2 shows, BPA concentration had a sharp drop in the first two minutes as well. These observations confirm the hypothesis of instantaneous reaction in the first two minutes in the liquid.

The second phase is from third minutes to about 10 minutes of reaction while the reaction is still very fast in this stage but most probably it occurs in the liquid film around gas bubbles because of accumulation trend of aqueous ozone in the reactor. This means that the reaction of primary aromatic compounds (BPA and its aromatic primary by-products) and dissolved ozone in water is moderate and no mass transfer limitation exists. In fact, reaction between BPA and primary aromatic intermediates occurs in the interface of liquid and gas films, but as ozone reacts with double bonds of aromatic by-products, more linear compounds are forming and dissolved ozone starts to accumulate and reach its stable amount in the system (comparable to concentration levels before adding BPA).

Finally the last stage of reaction is the reaction between linear by-products of BPA and dissolved ozone. This phase of the reaction is very slow and it occurs in the bulk of liquid.

Because of these three main stages of reaction in this system it is not appropriate to expect a single reaction rate constant during the mineralization of BPA. But in each of these three stages different kinetics approach can be considered. As it was discussed before in the introduction, the reaction of ozone with organic compounds in aqueous phase is very complex and many other species are involved in the real reactions, since ozone itself has a complex self-decomposition in aqueous phase (Equations 1.1 to 1.11). Therefore, to be able to study the behavior of system kinetically it can be assumed that only molecular ozone and OH radicals are oxidizing species towards organic compounds (Equation 1.11). So the TOC content of reaction solution can undergo two different reactions paths as below:

$TOC + O_3 \rightarrow$ products

$TOC + OH^{\bullet} \rightarrow$ products

Mainly, second-order reaction rate is considered for the reaction between ozone (and or $OH^{\bullet}$ radicals) and organic compounds in literature [9, 20, 24, 31]. Here a second order reaction between ozone and BPA and its by-products is used in this work. To be able to model reaction based on TOC removal which could include different species with different reactivities towards ozone, three main stages during ozonation of BPA were considered. Equation 6.2 represents the second order reaction rate equation for TOC and ozone.

$$-r_{TOC} = -\frac{d[TOC]}{dt} = k_{O3}\,[TOC][O3] + k_{OH^\bullet}\,[TOC][OH^\bullet] \quad (6.2)$$

And because the concentrations of OH radicals are proportional to concentration of ozone in the liquid we can assume that:

$$[OH] = \alpha\,[O_3] \quad (6.3)$$

Then equation 6.2 can be rewritten as below:

$$-r_{TOC} = -\frac{d[TOC]}{dt} = k_{O3}\,[TOC][O3] + k_{OH}\,[TOC]\,\alpha[O3] \quad (6.4)$$

$$-r_{TOC} = -\frac{d[TOC]}{dt} = (k_{O3} + \alpha\,k_{OH})[TOC][O3] \quad (6.5)$$

$$k_{obs} = (k_{O3} + \alpha\,k_{OH}) \quad (6.6)$$

So we have simply the influence of ozone in the reaction rate in the last equation:

$$-r_{TOC} = -\frac{d[TOC]}{dt} = k_{obs}\,[TOC][O3] \quad (6.7)$$

In order to calculate k_{obs} from Equation 6.7, we should integrate the Equation 6.8 as below:

$$\int_{[TOC]_0}^{[TOC]_t} -\frac{d[TOC]}{[TOC]} = \int_{t_0}^{t} k_{obs}\,[O3]dt \quad (6.8)$$

$$Ln\frac{[TOC]_0}{[TOC]} = \int_{t_0}^{t} \mathrm{k_{obs}}\,[O3]dt \qquad (6.9)$$

Now by plotting "$Ln\frac{[TOC]_0}{[TOC]}$" versus "$\int \mathrm{k_{obs}}\,[O3]dt$" observed reaction rate constant (k_{obs}) can be obtained. A numerical integration based on Trapezoidal rule was used to calculate "$\int \mathrm{k_{obs}}\,[O3]dt$" for different times of reaction. Then term "$Ln\frac{[TOC]_0}{[TOC]}$" was calculated by considering 7.8 ppm $[TOC]_0$ equal to 10 ppm $[BPA]_0$.

Figure 6.1 represents these three stages of reaction and their calculated reaction rate constants in BPA non-catalytic ozonation experiment. This observed reaction rate constant can provide us a good indication about the kinetics regime during TOC removal in different stages of BPA non-catalytic ozonation reaction.

As it is clear in Figure 6.1, k_{obs} is calculated by a linear fit of experimental data giving 112.1, 7.5 and 2.1 M^{-1} min^{-1} for first (0-2 min), second (2-10 min) and third (10-60) stage of reaction, respectively. Rivas et al. [20] used a similar approach for kinetics of TOC removal reaction in BPA non-catalytic ozonation reactions and reported about 9.5 M^{-1} min^{-1} for observed rate constant value after aqueous ozone was stabilized in their system which is in the range of rate constants for second and third stages (7.5 and 2.1 M^{-1} min^{-1}) in this work.

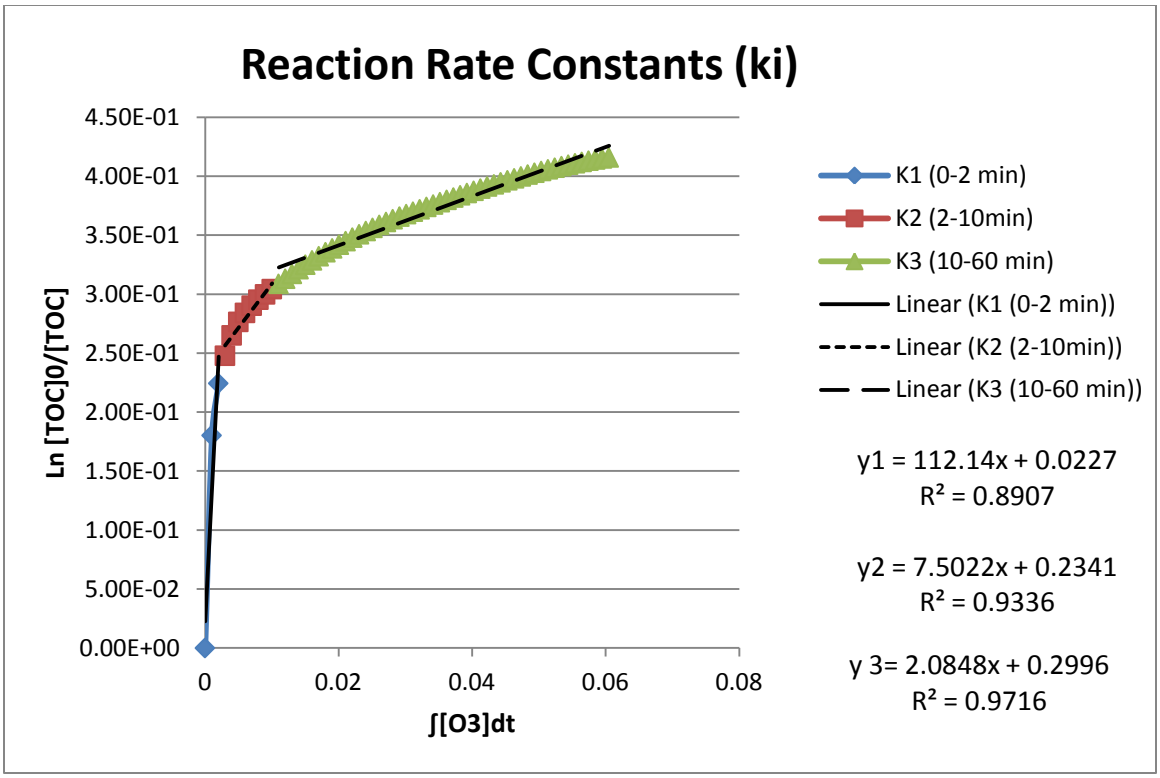

Figure 6.1. Reaction rate constants for non-catalytic ozonation of BPA based on TOC removal

($[BPA]_0$=10 ppm,$[O_3]_0$=4.5±0.5 ppm, pH0= 5.0 ± 0.2 , T=23±2 ˚C)

This kinetics approach is applicable to catalytic ozonation of BPA regardless of considering where exactly catalytic reaction took place and by using powder alumina catalyst which eliminates the mass transfer limitations. This method of modeling the reaction kinetics is not a representation of true kinetics of catalytic reactions and the k_{obs} values reported here are just quantities to provide a basis to compare the effect of using catalyst to enhance the reaction rate.

Figure 6.2 shows the Reaction rate constant for catalytic ozonation of BPA based on TOC removal with alumina catalyst. Similarly to non-catalytic ozonation, there are three stages in catalytic ozonation as well. As Figure 6.2 clears, applying catalyst to the system significantly

increased the reaction rate towards TOC. The values of k_{obs} for first, second and third stages of reaction were calculated as 4889.8, 695.3 and 291.1 M^{-1} min^{-1}, respectively.

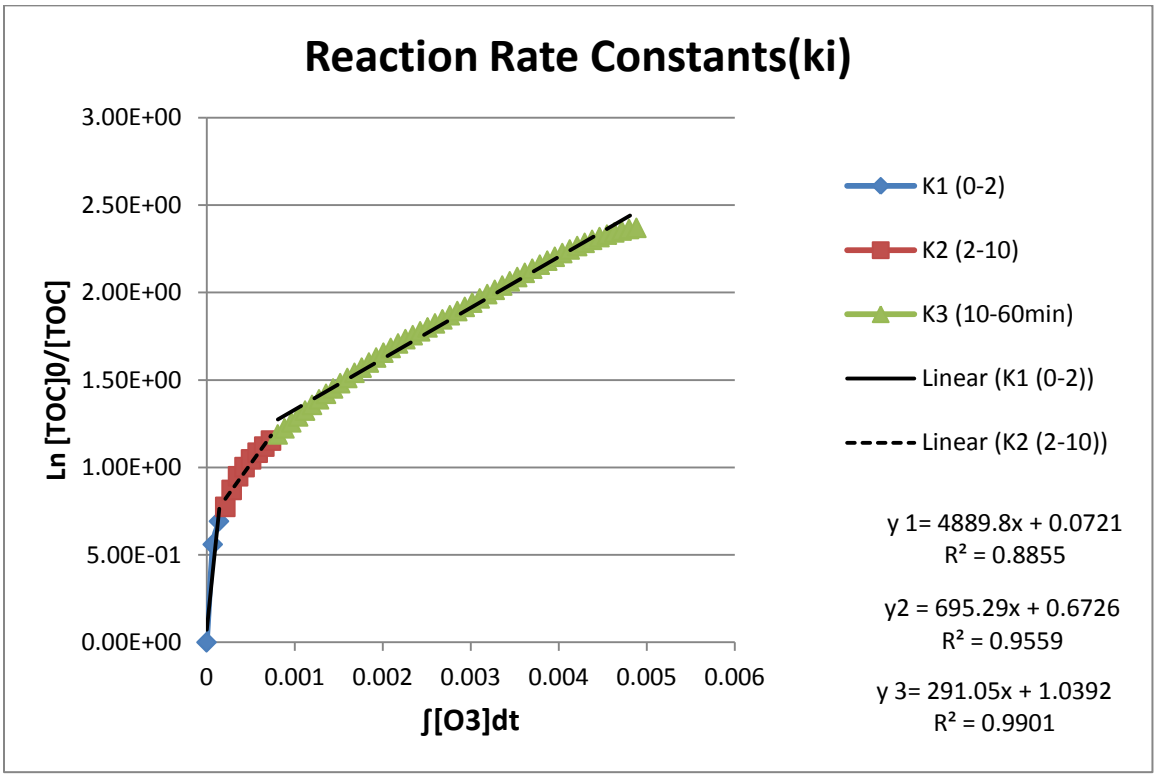

Figure 6.2. Reaction rate constants for Catalytic ozonation of BPA based on TOC removal with alumina catalyst ($[BPA]_0$=10 ppm,$[O_3]_0$=4.5±0.5 ppm, pH0= 5.0 ± 0.2 , T=23±2 ˚C, particle size of catalyst <0.23 mm and dose of catalysts= 1 g/ L)

The values for k_{obs} can be compared stage by stage for catalytic experiment to non-catalytic experiment of BPA and ozone, as 43 to 1 for first stage, 92 to 1 for the second stage and 138 to 1 for the third stage of reaction. Clearly the most significant effect of applying alumina in enhancing reaction rate is catalyst effect in enhancing the third stage of the reaction. It is in

agreement with our previous discussion about high reactivity of ozone with phenolic rings of BPA. Alumina catalyst in the beginning of reaction did not have strong effect because ozone itself was reacting and consuming the phenolic rings but as other by-products were forming accumulated (unreacted) ozone had more interaction with catalyst surface. So the increasing trend of reaction rate constant ratio (catalytic to non-catalytic) can be explained by this fact. Table 6.1 summarizes the reaction rate constants for non catalytic and catalytic ozonation of BPA.

Table 6.1. Reaction rate constants for non catalytic and catalytic ozonation of BPA

Experiment	$\mathbf{k_{obs1}}$ (M^{-1} min^{-1})	$\mathbf{k_{obs2}}$ (M^{-1} min^{-1})	$\mathbf{k_{obs3}}$ (M^{-1} min^{-1})
Non-catalytic ozonation	112	7	2
Catalytic ozonation (alumina)	4889	695	291
Non-Catalytic Ozonation (Rivas et al. 2009)	-	-	9

6.2. Mass transfer in catalytic ozonation of BPA

In an attempt to study the effect of alumina catalyst for BPA mineralization in the ozonation systems, in a very simple step, observed rate of reaction can be defined to study the actual rate of reaction. The observed reaction kinetics for reaction between TOC of BPA and ozone can be defined by the first part of Equation 6.2 and can be written as below:

$$-r_{TOC} = \frac{d[TOC]}{dt} \tag{6.10}$$

According to Equation 6.10, the observed rate of catalytic ozonation reactions in the presence of different particle sizes of alumina catalyst can be determined by finding the derivatives of the TOC profile as a function of time.

Figure 6.3 shows the calculated $-r_{TOC}$ in the presence of different catalyst particle sizes. As can be seen, the trends of the reaction rate confirm the fast nature of reaction between ozone and TOC in the presence of alumina catalyst with variety of particle size, specifically in first 10 min of reaction. Although the difference between reaction rates is very clear at the beginning of the reaction, there is no significant variation in the reaction rate by changing the catalyst particle size for the rest of reaction time after 10 minutes.

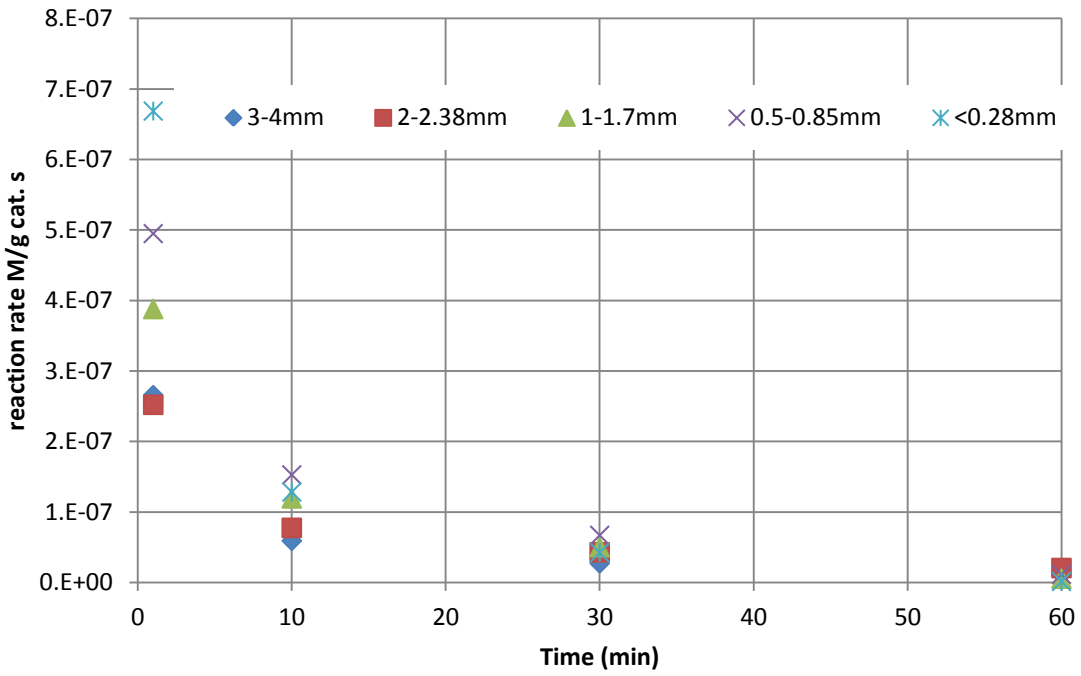

Figure 6.3. Effect Observed reaction rate of catalytic ozonation in the presence of alumina with different particle sizes ($[BPA]_0$=10±1 ppm, $[O_3]_0$= 4.5±0.5 ppm, pH_0= 5.0 ± 0.2 , T=23±2 ˚C, dose of catalysts= 1 g/ L)

Based on the initial rate of reaction for different catalyst particle sizes, we can define effectiveness factor for the reaction on each catalyst. Equation 6.11 as below shows the concept of effectiveness factor:

$$\eta = \frac{\text{actuall overall rate of reaction}}{\text{rate of reaction that would result if entire interior surface were exposed to the external surface conditions}} = \frac{-r_A}{-r_{As}} \qquad (6.11)$$

In this work one can assume $-r_A$ the observed reaction rate in the specific particle size and $-r_{As}$ the observed reaction rate for powder catalyst. Then based on this definition one can calculate $\boldsymbol{\eta}$ as 0.74, 0.58, 0.38 and 0.37 for 0.5-0.85 mm, 1-1.7 mm, 2-2.38 mm and 3-4 mm particle size of alumina catalyst, respectively. The term effectiveness factor ($\boldsymbol{\eta}$) contributes to how far the reactant diffuses into the pellets before reacting, so as expected, by decreasing the particle size the effectiveness factor increases. In other words, when $\boldsymbol{\eta}$ is high the reaction is less limited by diffusion and the reason that this factor is 1 for powder size is that the reaction is not limited by particle diffusion but is surface-reaction limited [42].

The same procedure as particle size actual reaction rate has been repeated in the case of alumina catalyst dosage. Figure 6.4 provides the variation of reaction rate with time for different catalyst dosages.

As Figure 6.4 indicates, the rate of TOC removal in the presence of catalyst is very fast at the beginning and drastically drops after 10 minutes. Although, the reaction rate exhibits a high dependency on the catalyst dosage in the first 10 min, it does not seem to be affected by the amount of catalyst for the rest of reaction time. Thus, increasing the catalyst dosage cannot lead to 100% TOC removal.

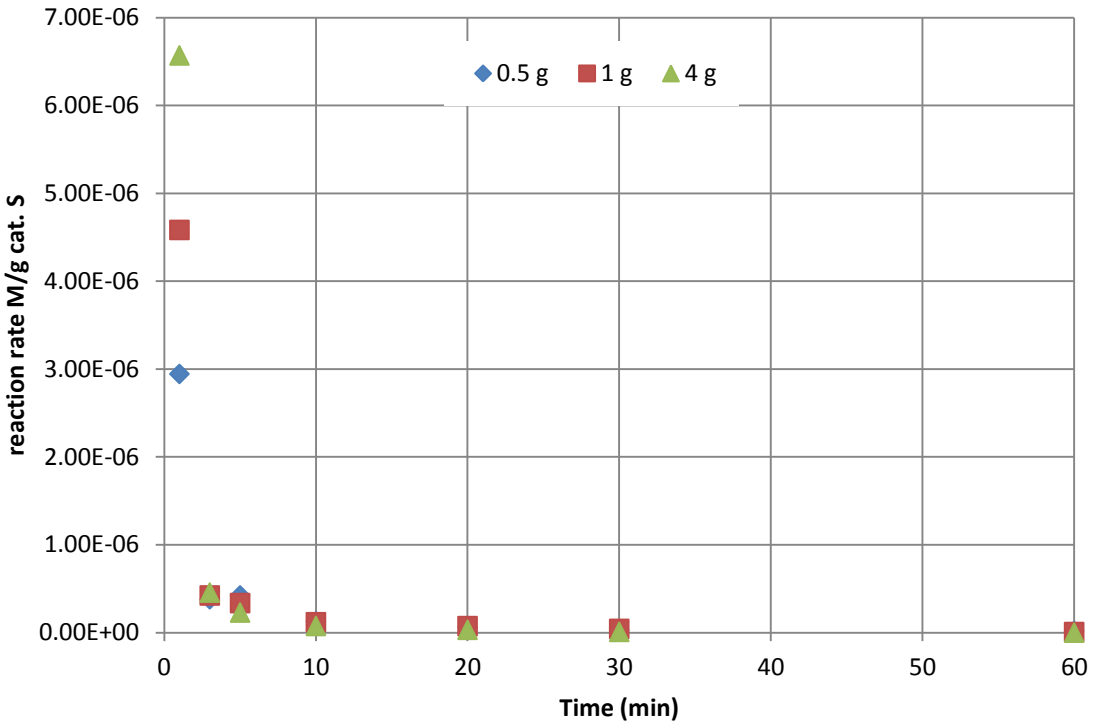

Figure 6.4. Observed reaction rate of catalytic ozonation in the presence of alumina with different dose ($[BPA]_0$=10±1 ppm, $[O_3]_0$= 4.5±0.5 ppm, pH_0= 5.0 ± 0.2 , T=23±2 ˚C, particle size of catalyst<0.23 mm)

6.3. Summary and conclusions

The study of kinetics of TOC removal was essentially used to develop a better understanding of different stages of TOC removal during ozonation processes.

- TOC removal has three stages from the kinetics point of view both in non-catalytic and catalytic ozonations, fast reaction with a very high reaction rate constant, fast reaction with intermediate rate constant and finally slow reaction with very low rate constant.

- The same trend of non-catalytic ozonation of BPA has been observed in the kinetics regime of catalytic ozonation but alumina catalyst had a significant effect on rate constant of ozonation of BPA (almost an order of magnitude).

CHAPTER 7

TOXICOLOGY OF BPA OZONATION

As it is mentioned in literature review, evaluating estrogenicity of treated samples is an important step to make sure that mineralization of BPA has been achieved and no harmful materials remained in the final solution. Since BPA is an endocrine disrupting compound, the first priority is testing its estrogenicity which reveals information about the endocrine disrupting features of solution.

7.1. Evaluation of estrogenicity

As it can be seen in Figure 7.1 the baseline of samples which is Millipore water considered 100 % and by adding BPA to this pure water to reach 10 ppm concentration this baseline of estrogenicity increase to over 240 %. Then in next step, this 10 ppm BPA sample was ozonated for 60 minutes under reaction conditions of ,$[O_3]_0$=4.5±0.5 ppm, pH_0=5.0 ± 0.2 and T=23±2 ˚C. Estrogenicity of BPA sample after ozonation was reduced from initial 240% to 175% indicating the efficiency of ozone as an oxidant in reducing the estrogenicity of samples. However, ozone

alone is not able to reduce estrogenicity of BPA to below baseline, so combination of this process with a suitable catalyst could possibly lead to even more estrogenicity removal. In this work alumina as an active catalyst was added to the reaction mixture under the same reaction conditions as sole ozonation in amount of 1 gL^{-1}. As it is clear in Figure 7.1, addition of alumina has a positive impact in removing estrogenicity of BPA and reducing it to the baseline level. Combination of alumina catalyst and ozonation is a very promising approach to reduce the estrogenicity of BPA to baseline.

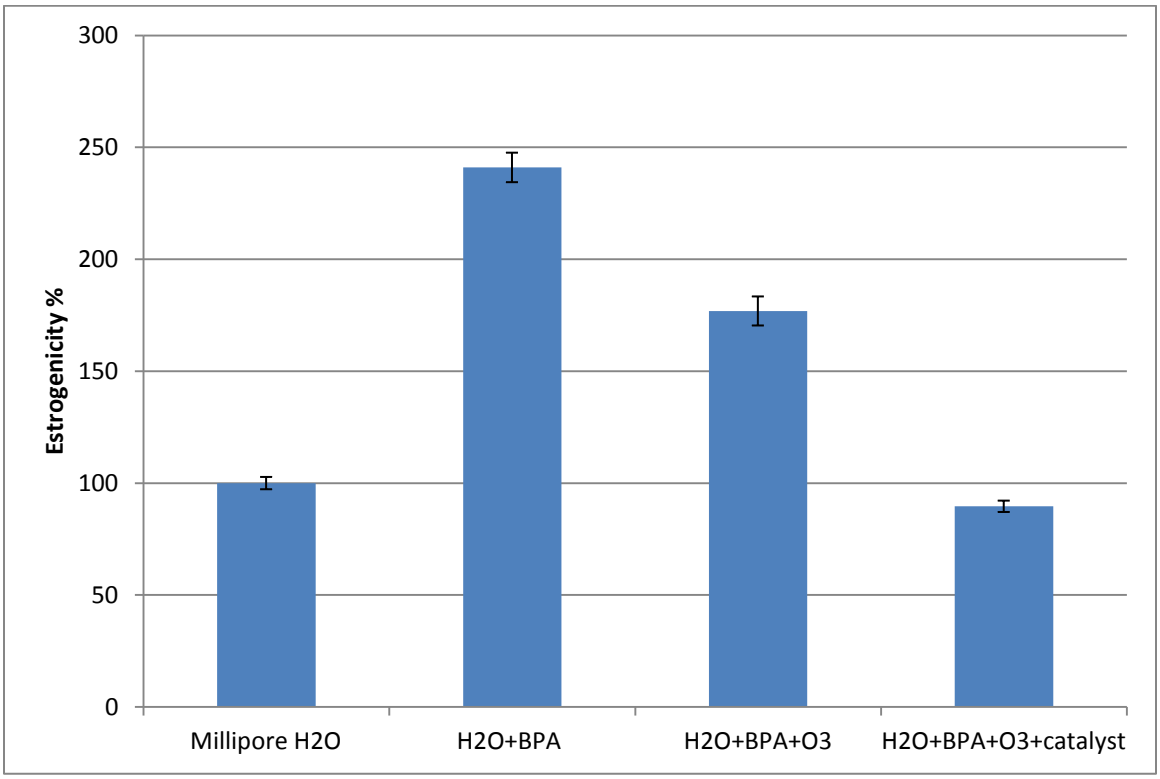

Figure 7.1. Percent of estrogenicity of BPA samples, as baseline in Millipore water without adding BPA, BPA aqueous solution of 10 ppm, ozonation of BPA sample and Catalytic ozonation of BPA, reaction conditions $(BPA]_0$=10±1 ppm,$[O_3]_0$=4.5±0.5 ppm, pH_0= 5.0 ± 0.2 , T=23±2 ˚C and 1 gL^{-1} in case of catalytic experiments).

7.2. Evaluation of cytotoxicity

Also, it is important to examine that none of the involved chemicals in samples are toxic to MVLN cells. In order to check this important factor, series of cytotoxicity tests were performed in all cases of our study, Millipore water, BPA solution, ozonated BPA solution and finally catalytic ozonation of BPA solution. Figure 7.2 shows the result for cytotoxicity over a 24-hour exposure for all of the samples. As it is clear in the Figure 7.2, test conditions in each stage of experiments are completely non-toxic to cells and all of the conditions showed the viability.

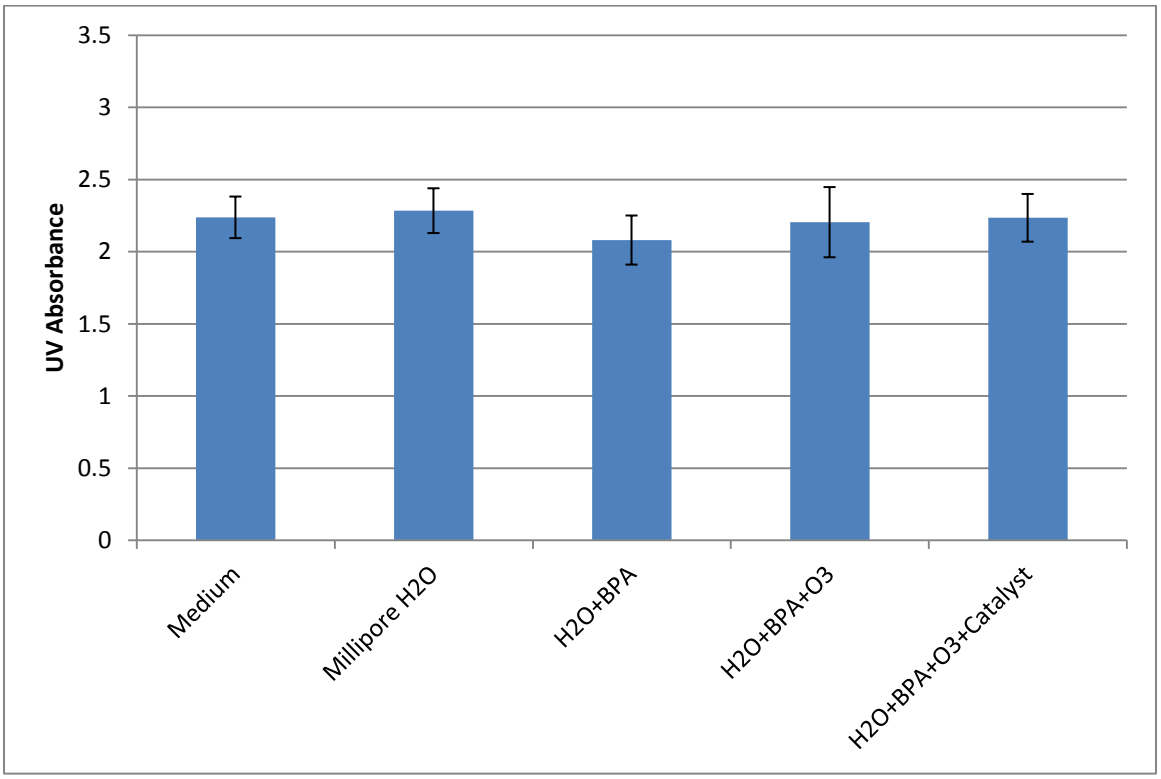

Figure7.2. Cytotoxicity of BPA samples, reaction conditions $(BPA]_0$=10±1 ppm,$[O_3]_0$=4.5±0.5 ppm, pH_0= 5.0 ± 0.2 , T=23±2 ˚C and 1 gL^{-1} in case of catalytic experiments).

7.3. Summary and conclusions

The result for estrogenicity and cytotoxicity of samples showed that:

- Ozone was able to reduce the estrogenicity of BPA solution by about70% from 242% for untreated BPA sample to 174% for ozonated BPA sample.

- Ozonation in the presence of 1 gL-1 alumina, significantly improved estrogenicity reduction to about the baseline, Milli-Q water of about 90%.

- Finally, cytotocicity test showed that none of the materials used in our experiments were toxic to the cells used in estrogenicity tests.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

The most important result of this work is demonstration of positive role of each of used catalyst in mineralization of BPA with ozone. Different aspects of the processes were explored by running experimental plans such as non-catalytic ozonation experiments, adsorption on surface of catalysts, ozone decomposition, catalytic ozonations including particle size and dosage effects, reusability, and toxicity studies.

From non-catalytic ozonation it was learned that different factors including BPA and ozone initial concentrations, pH and temperature affect BPA mineralization. Under the best reaction conditions a 35% BPA mineralization was attained.

By performing blank tests of BPA adsorption and ozone decomposition, it was concluded that activated carbon is a very good adsorbent with almost 90% TOC removal in the absence of ozone. Both alumina and Mn-alumina were poor adsorbents towards BPA. Catalytic ozonation with alumina and Mn-alumina catalysts showed promising results for mineralizing BPA to harmless compounds by 90% TOC removal. Particle size of alumina had a strong effect on

mineralization of BPA due to mass transfer limitations but dosage of alumina did not have a significant effect on the process. In case of by-products adsorption, although the result showed a very high affinity of alumina to adsorb by-products, the catalyst showed negligible amount of adsorbed carbon on its surface that could be an advantage of catalytic ozonaion for adsorption of by-products.

Alumina catalyst did not showed any deactivation after three consecutive cycles in the presence of ozone in catalytic process of BPA mineralization. However, alumina catalyst which showed a very high adsorption of by-products in the absence of ozone failed to serve as a long term adsorbent without oxidizing agent, ozone. So finally it could be conclude that alumina is a better material as a catalyst in the presence of ozone.

The recommendations for future work are:

- Ozone and specifically catalytic ozonation proved to be effective methods to eliminate micropollotant from pure water, but in order to evaluate the process under more realistic applications, it is recommended to study the effect of water matrices such as river water or treated waste water on catalytic processes.
- It is recommended to conduct ozonation processes in the continuous mode instead of having a limited micropollutant in semi batch mode.
- It is recommended to use a fixed bed reactor rather than a slurry reactor for study of the reaction. This will make real cases studies even easier since many problems of catalysts separation from solution will be eliminated. This is crucial, especially in reusability cycles experiments.
- Identification of some major by-products will help to develop a better kinetics model in the case of TOC of ozonated and catalytic ozonated BPA.

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